THE TEXT IS
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IRON AND STEEL DIVISION
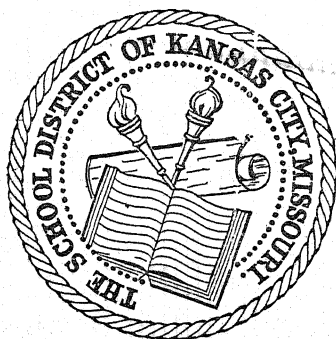
DIVISION

1931

TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

IRON AND STEEL DIVISION

1931

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT
MEETINGS HELD AT NEW YORK, FEBRUARY, 1931, AND AT
BOSTON, SEPTEMBER, 1931

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Notice

This volume is the fourth of a series containing papers and discussions presented before the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers since its organization in 1928; one volume each year, as follows:

1928, Iron and Steel Technology in 1928
1929, 1930 and 1931, Transactions of the American Institute of Mining and Metallurgical Engineers, Iron and Steel Division

This volume contains papers and discussions presented at the New York Meeting, Feb. 16–19, 1931, and the Boston Meeting, Sept. 21–25, 1931.

Papers on iron and steel subjects published by the Institute prior to 1928 are to be found in many volumes of the TRANSACTIONS of the Institute; during the past 25 years in Vols. 37 to 45, inclusive; 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive; 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS may be found by consulting the general indexes to Vols. 1 to 35 (1871–1904), Vols. 36 to 55 (1905–1916), and Vols. 56 to 72 (1917–1925), and the indexes in succeeding volumes.   Reference

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CONTENTS

The Howe Memorial Lecture

THE Howe Memorial Lecture was authorized in April, 1923, in memory of Henry Marion Howe, as an annual address to be delivered by invitation under the auspices of the Institute by an individual of recognized and outstanding attainment in the science and practice of iron and steel metallurgy or metallography, chosen by the Board of Directors upon recommendation of the Iron and Steel Division

So far, only American metallurgists have been invited to deliver the Howe lecture. It is believed that this lecture would gain in importance and significance were it possible to include metallurgists from other countries, but the Institute has not yet been able to do this on account of lack of special funds to support this lectureship

The titles of the lectures and the lecturers are as follows

1924   What is Steel?   By Albert Sauveur

1925   Austenite and Austenitic Steels   By John A Mathews

1926   Twenty-five Years of Metallography   By William Campbell

1927   Alloy Steels   By Bradley Stoughton

1928   Significance of the Simple Steel Analysis   By Henry D Hibbard

1929   Studies of Hadfield's Manganese Steel with the High-power Microscope   By John Howe Hall

1930   The Future of the American Iron and Steel Industry   By Zay Jeffries

1931   On the Art of Metallography   By Francis F Lucas

1932   The lecturer will be Edgar C Bain, the title of the lecture, On the Rates of Metallurgical Reactions in Solid Steel

FOREWORD

It is a pleasure to record for this particular year—not to stress a slight increase in membership—marked progress by many of the committees of the Iron and Steel Division   This progress is exemplified in divers ways, but an important part is represented by the present volume

The Open Hearth Conference has had an exceptionally successful history   To some it therefore occurred. Why not a Blast Furnace Conference?   Under the leadership of Col F B Richards and Mr C B Murray, a Blast Furnace Conference is well along in the process of formation

Another constructive step is the result of a preliminary investigation by the Institute's Committee on Correlation of Research under the chairmanship of Dr A C Fieldner   This past summer a recommendation was submitted to the effect that the Institute of Metals Division and the Iron and Steel Division endeavor to establish cooperative research under the broad title "Gases in Metals"   A committee is organizing a technical session on this subject, for the annual meeting next February   After the meeting definite proposals will be made for coordinated research in the nonferrous and ferrous metal industries

The original work recounted by Dr Francis F Lucas in his Howe Memorial Lecture created widespread interest   Dr Lucas has blazed a trail for metallographists, the results of which no doubt will be far-reaching in practical importance, furthermore, his exposition of the possibilities inherent in high-power microscopy has given notable impetus to biologists and other scientists

The Science Lecture delivered at the Boston Meeting on September 24 was an innovation   Dr P W Bridgman chose for his subject "Recently Discovered Complexities in the Properties of Simple Substances"   Highly technical, to be sure, but conducive to much thought by modern metallurgists, our first Science Lecture established an excellent standard   (The lecture will appear in the last volume of TRANSACTIONS published this year)

It is not immodest to state that the Boston Meeting, held late in September under the joint auspices of the Institute of Metals Division and the Iron and Steel Division, brought forth so much enthusiasm as again to make apparent the desirability of fall meetings as a regular part of the yearly program   And this opportunity is taken to say that the cooperation of the Institute of Metals Division has been truly a joy at all times

The meetings held annually on the evenings preceding the spring and fall meetings of the American Iron and Steel Institute have always been enjoyable and instructive The evenings are devoted largely to informal discussions of many subjects In the present year several most interesting descriptions were received relating to metallurgical operations in foreign countries

The progress of the Division is the result of the combined efforts of the Vice-chairmen, members of the Executive Committee, the Secretary, and the members of the technical committees, to whom sincere appreciation is expressed

From the President of the Institute, Mr Robert E Tally, from Dr H Foster Bain, Secretary, and from Mr A B Parsons, Assistant Secretary, much invigoration has been received   To them we are indebted

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* Mr Bain resigned as Secretary, in the fall of 1931, and Mr Parsons was appointed by the Directors to that office The change went into effect on November 1

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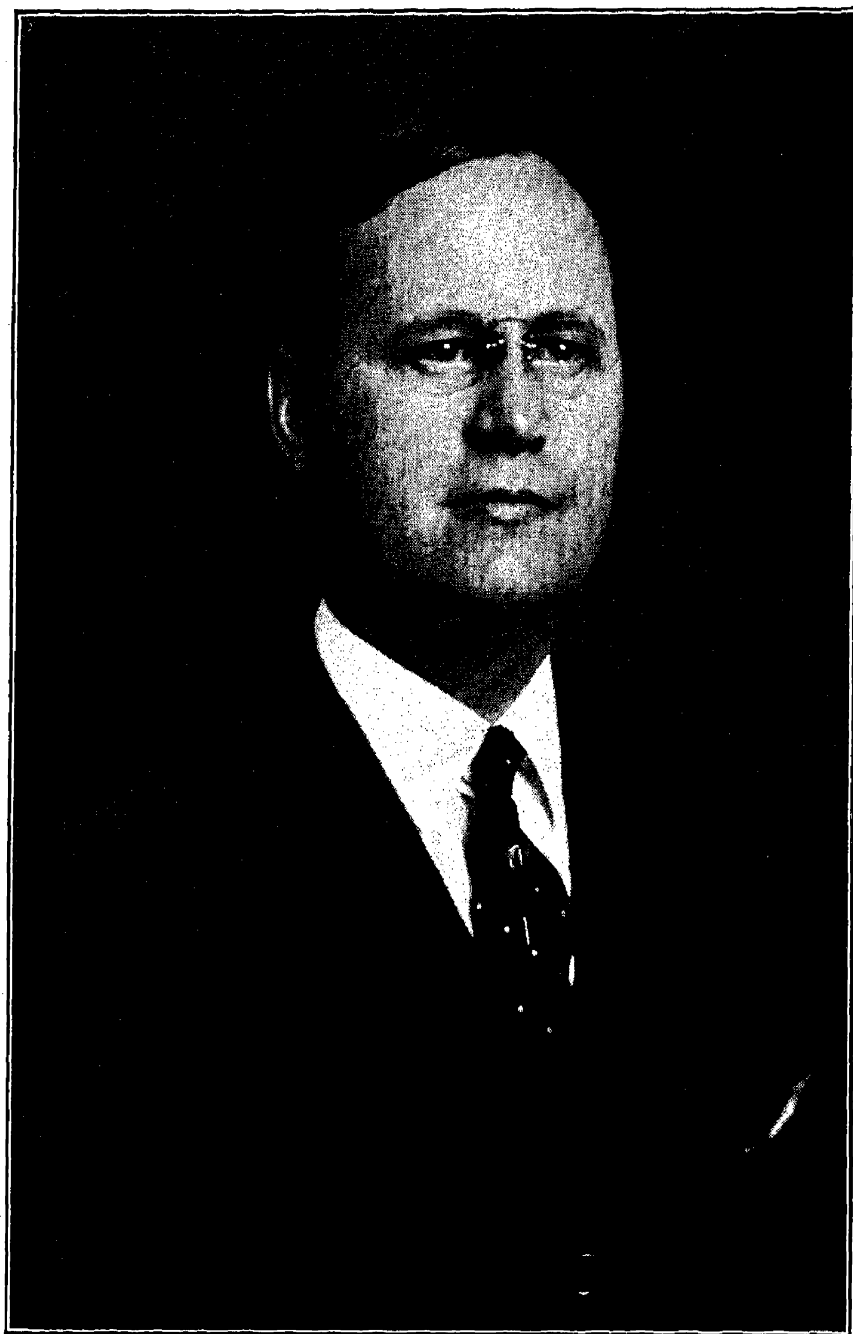
FRANCIS F. LUCAS
Henry Marion Howe Memorial Lecturer, 1931

On the Art of Metallography

By Francis F Lucas,* New York, N Y

(Henry Marion Howe Memorial Lecture †)

Each year we gather in this auditorium to honor the memory of a distinguished American metallurgist and educator   I cannot bring to you reminiscences of Prof Henry Marion Howe as other lecturers have done   It was not my good fortune to enjoy the privilege of studying and working under his direction   As I have reflected on the published works of Professor Howe, it has seemed to me that his mind was trained on the nature of metals and on the mechanism which produced known but unexplained effects   He was interested in controlling and regulating the causes so as to produce specific effects, useful in serving mankind

I recall an afternoon in May, 1925, when, at the invitation of Mrs Howe, I visited his former home, Green Peace at Bedford Hills, N. Y The purpose of my visit was to receive at the hands of the widow an engraving of Professor Howe, a reproduction of a painting from life Mrs Howe showed me his study   The walls of this large attractive room, brilliantly illuminated by the spring sunshine, were literally covered with the scrolls of honors and of decorations which had been conferred on Professor Howe by governments, academies, universities, societies and institutions the world over   As we walked about the room, she pointed out the significance of each honor and recited a few details of each occasion   I sensed the pride with which Mrs Howe, then in the late autumn of her life, told me of her husband's achievements, of his struggles, of his disappointments and of his successes   There was a surprisingly familiar note in the recital to which I was listening   I have found the same theme running as a disconnected thread through the written accounts of the lives of most men of science

We then went to the drawing room to chat for a few minutes before I said my farewells   As we seated ourselves, Mrs Howe turned to me and asked

"Mr. Lucas, what of this great microscope of yours?   Cannot it be applied to the study of disease?   What a great blessing it would be if it could be directed to relieve the suffering of mankind "

Mrs Howe was among the very first to surmise that a tool developed in metallurgical circles might have far greater usefulness in a field almost

wholly unrelated to the science of metallography   I do not recall that her remarks impressed me.   There appeared to be no immediate application   Twenty-five years before this time, the ultra-violet microscope was developed for biological research.   At that time, metallography was in its infancy   For many years ultra-violet microscopes have lain unused, collecting dust in out-of-the-way corners of biological laboratories here and there throughout the world, a scientific curiosity seemingly of no practical use

In learning how to use the equipment as a metallurgical microscope, certain inherent possibilities of the ultra-violet system were discovered These were discoveries which since have made it possible to photograph the internal architecture of living cells, figuratively speaking, to place the microscope within a single living cell, itself microscopic in size, and to take photographs at very high magnifications of the structure within the cell—to photograph upward or downward on different planes spaced 0.00001 in apart   In some cases, as many as 20 or 30 photographs may be taken on as many different optical planes within the cell, and generally without interfering, so far as one is able to detect, with the normal living functions of the cell   These methods bring within photographic range the structures of living things in a manner never before possible.

A tool of great potential possibilities is developed for one branch of science   It is not a success and it is practically abandoned   After a quarter of a century has elapsed, it is revived in another branch of science, its possibilities developed and set to work in the original field for which it was intended.

It seems likely that Mrs Howe's expression of hope may be realized Who is there who says science is lacking in romance?

It is not of these things that I would speak to you, nor shall I present some bit of metallurgical research at this time   It has seemed fitting to discuss some of the fundamentals which I have found useful in my work in the hope that the views expressed may be of interest, particularly to the young men of industry who will follow in the science of metallography

You and I are metallurgists in one sense of the word or another   If you happen to be a metallographer, then you and I deal in the structure of metals because we have learned that the physical properties of metals and their structure go hand in hand   Though we have not always been able to associate a change in structure with a change in physical properties, nevertheless we have been convinced in our own minds that if we could see the structures more clearly, we would know what it is that causes the good or poor physical properties and in future we could aim to promote or avoid such structures

Nowadays those who use microscopes expertly know little about the design and the construction of the optical parts and the associated apparatus   Their interest lies almost solely in the use of the equipment   The

designer and the optician, on the other hand, are not experts in the exami-
nation of materials   This is the job of the microscopist   Their job is
primarily that of the mathematician and the physicist   They are con-
cerned with the behavior of light as it is refracted and their energies are
directed toward the production of less faulty images, since all optical
images are more or less imperfect   Each vocation in itself is a life study
but each group of workers knows a little of the others' work, so that there
is an overlapping

It would be presumptuous for me to attempt a discussion of problems
relating to the work of the optician or the designer; but if we are to use
our tools intelligently, we must know something of the principles on which
they are constructed   At least we should have sufficient knowledge to
put them to critical test   We shall not know whether one objective is
better than another—whether one is functioning perfectly or imper-
fectly—unless it shall be judged by test or by opinion or by both   Opin-
ion is valuable only because of the experience on which it is based

We shall consider only the phase of metallography which consists in
achieving crisp, brilliant images at very high magnifications and in
achieving approximately the full potential resolving ability of the best
optical systems   Very likely you will fail to find the term "potential
resolving ability" defined in books on optics and physics   It implies
that the ability to do certain things is an inherent but hidden character-
istic of the system   It requires directive force, imagination, artistic
sense, technique and experience to get it out   A fine musical instrument
in the hands of a novice may mean a riot call for the police but the
same instrument in the hands of a master can hold a vast audience at
hushed attention

It implies that when you purchase an equipment consisting of a
microscope and associated optical parts for metallography, you are enter-
ing into a partnership   You are the senior partner, the one who decides
what shall be done, and the success of the business, which is photo-
graphing metal structures, will depend first on yourself and second on the
optical parts   If wisely selected, the optical parts when associated as a
system have certain potential possibilities of a high order   If you are the
kind of a partner who has talent, if you have imagination, if you can face
discouragements, you will discover that these potential possibilities mean
something.   Your contribution to the firm will decide whether the
potential resolving ability or only the magnifying ability will be realized
in practice.

Let me restate this partnership idea in another way because the
importance of the meaning which it conveys cannot be overemphasized
The young metallographers of industry will learn by experience that the
results they produce are largely dependent on their own aptitude for the
work—on the care and thoroughness with which they apply themselves

The executives of industry, however, who provide the funds to buy the equipment and to develop talent, may fail to appreciate the fine points of the game   Often they expect results overnight.   It will do no harm to say a few additional words in behalf of the metallographers

It is common knowledge that the possession of oils, colors, brushes and the other working tools of an accomplished artist will not insure a masterpiece from one who is not thoroughly schooled in art   We could all become great artists if that alone were all that is required.   And you may be equally sure that possession alone of fine optical equipment will not enable one to go closer visually to the ultimate structure of matter than human eye has ever gone before.

To follow expertly this highway of research with the microscope is almost the task of a lifetime but it leads into a universe which rivals in fascination anything that a Jules Verne could imagine   Once established within the confines of this universe, you see the way in which nature builds and tears down   The most commonplace metals have intricate riddles to be solved and, in the realm of living things, the field of possibilities is almost too great to contemplate

OPTICAL SYSTEM OF THE COMPOUND MICROSCOPE

There is a basic fact lying back of the images formed by a compound microscope   The objective of the microscope forms an image of the object and this image in turn is enlarged or magnified by the ocular   If we wish to improve the quality of the image or if we wish to increase resolving ability, it is to the objective that we must direct attention No eyepiece or optical combination taking the place of the eyepiece can possibly furnish detail which originally is not present in the image formed by the objective

MICROSCOPE OBJECTIVES

Objectives are of four general classes achromatic, semi-apochromatic, apochromatic and monochromatic   The fundamental difference between a dry objective and an immersion objective is one of resolution   An immersion objective has greater light-gathering power than a dry lens of corresponding focal length   This light-gathering power is expressed by the numerical aperture

Numerical Aperture

Fig. 1 shows the conditions prevailing in a metallurgical microscope where light is directed by suitable means to the prepared surface of the specimen which it illuminates   Two rays, such as ray 1 and ray 2 leaving the object at the same angle, will behave quite differently.   Ray 2 is refracted by the immersion oil or bent inward.   Ray 1, which is pictured

to show the conditions without immersion oil, just enters the front lens of the objective It is obvious that other rays leaving at a greater angle than ray 2 will also be bent inward and some extreme ray, such as ray 3, will just enter the front lens of the objective Thus an immersion objective has greater light-gathering power than a dry objective This light-gathering power or numerical aperture supplies a measure for
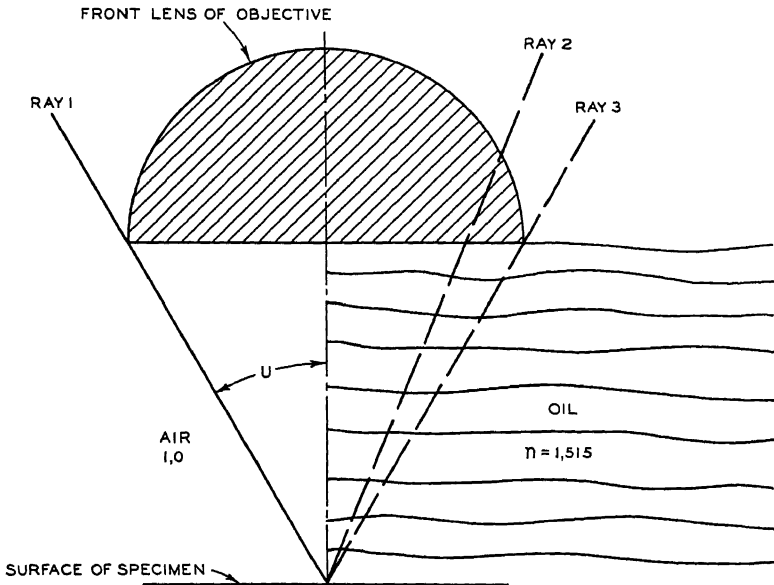
FIG 1 —ILLUSTRATING NUMERICAL APERTURE AND SUPERIOR LIGHT-GATHERING POWERS OF AN OIL-IMMERSION OBJECTIVE REFLECTED LIGHT

several essential qualities of an objective Professor Abbe, who first defined the conditions, expressed the relationship by the formula

$$NA = n \sin U$$

where n is the refractive index of the medium contained between the specimen and the front lens of the objective and U the semi-apertural angle of the system

The resolving power of the objective is directly proportional to the numerical aperture and the brightness of the image to the square of the numerical aperture As the numerical aperture increases, the depth of penetration (i e , the power of the objective to resolve detail simultaneously at different depths or distances from the objective) and the flatness of the field both decrease

TESTING OBJECTIVES

A critical purchaser of power apparatus does not confine acceptance or performance tests to reading of name-plate data He makes tests for

himself. He may make periodic tests to see that his apparatus is performing properly. It is equally important that the metallographer should know how to test his objectives, for the educational value of such observations, if for no other reason.

If what I say on this subject of testing objectives appears abstract and uninteresting or seemingly of little practical use to the metallographer, I can only apologize by reminding you that the objective is the key to metallography. What I shall say is neither new nor original. It is as old, almost, as the objective itself and has been repeated many times. Those who go far will need information on this subject. My brief remarks may provide the stimulus to search for better and for more complete information. I shall hardly more than direct attention to certain means for studying the behavior of objectives.

Tests with the Apertometer

The numerical aperture of an objective may be determined in several ways; one of the most convenient is by means of the Abbe apertometer (Figs. 2 and 3). This instrument consists of a semicylindrical plate
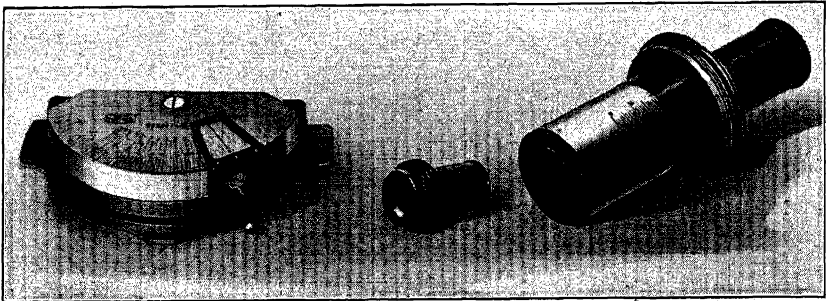
FIG. 2.—PARTS OF ABBE APERTOMETER.

of optical glass with two scales engraved on its upper surface. A revolving arm bearing a target with cross lines revolves in close contact with the cylindrical wall of the plate. Near the middle of the straight edge of the plate is a circular disk of silver which has a small slit. An auxiliary objective is screwed into the thread at the lower end of the microscope draw-tube.

In operation, the plate is placed upon the stage of the microscope, and the objective of which the aperture is to be measured is focused on the small slit in the circular disk of silver, using any convenient eyepiece. Illumination of the slit is secured by directing diffused light toward the cylindrical wall of the plate. After the objective has been focused, the draw-tube of the microscope is carefully removed and the auxiliary objective screwed into position. The draw-tube is then replaced and a

Huyghenian eyepiece is inserted. The draw-tube now becomes an auxiliary microscope for viewing the back lens of the objective. The cross lines of the target are sharply focused by sliding the draw-tube in or out within its collar. Measurements are made by displacing the target along the periphery of the plate until the cross lines just touch the boundary of the circle of light.

Fig. 4a is a diagram illustrating what one sees through the microscope when focused on the silver slit of the apertometer. Figure 4b illustrates
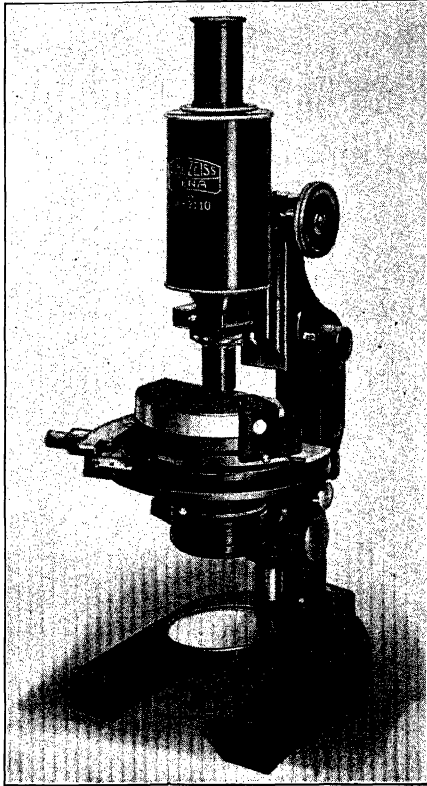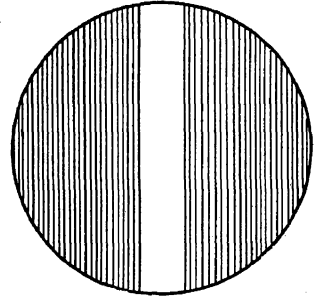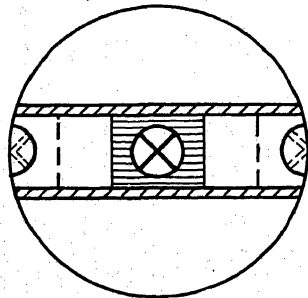
FIG. 3. FIG. 4.

FIG. 3.—ABBE APERTOMETER ASSEMBLED FOR USE.
FIG. 4.— TESTING NUMERICAL APERTURE OF OBJECTIVES WITH AN ABBE APERTOMETER.
    a. Silver slip of apertometer as viewed through microscope. b. Back lens of objective as viewed through auxiliary microscope. Cross hairs are displaced to right and left and scales of apertometer are read. Mean of readings is numerical aperture of objective.

how the back lens of the objective appears when looking through the auxiliary microscope. The target should be displaced both to the right and to the left and the mean of the readings of the outer peripheral scale gives the value of the numerical aperture of the objective under test.

The mean of the readings of the inner scale gives the values of the apertures in terms of the air angles

Color Correction of Objectives

The numerical aperture of an objective does not disclose information concerning the chromatic or spherical corrections which have been applied to the objective. The value of an objective also depends on the degree to which aberrations inherent in a simple lens have been corrected

In the achromatic objectives, the correction is least perfect of all and in the apochromatic objectives, the correction is of the highest order The semi-apochromatic objectives, as their name implies, occupy a position about intermediate No lens system, we are taught, is perfect All have some imperfections in the fusion of the rays

The achromat is an objective which is designed for visual work It is corrected to work at its best with the particular color of light which is most luminous to the eye Physiologically the most effective rays are the yellow green In this region of the spectrum the corrections of the objective are at their best and this color is referred to as the preferred color

The achromats are corrected chromatically for two colors and spherically for one color As the extremes of the visible spectrum are approached, the fusion of the rays becomes less and less complete When an achromat objective is properly corrected, residual colors of the secondary spectrum remain.

Apochromatic objectives are corrected chromatically for three colors and spherically for two and the fusion of the rays is more nearly perfect The colors of the secondary spectrum are eliminated altogether in a good objective and only a faint tertiary spectrum remains as residual color Objects are rendered in their natural colors with apochromatic objectives

The semi-apochromatic objectives occupy a position intermediate to the achromatic and the apochromatic Their correction is better throughout than that of the achromatic objectives although they are corrected in the same general way The residual color of the secondary spectrum, which is always characteristic of the achromatic and semi-apochromatic objectives, makes it necessary to use a filter which will exclude all secondary images when photographing with these objectives

Testing Objectives with the Abbe Test Plate

For the purpose of testing the correction of microscope objectives for spherical and chromatic aberrations, we may use a prepared test object of maximum contrast It takes the form of a crude ruling or grating and is known as the Abbe test plate

The Abbe test plate is supplied by Zeiss The instructions furnished with the instrument are very helpful It will suffice here to

explain the principles   The test plate will be of interest to metallographers as a means for testing and studying some characteristics of immersion objectives

The Abbe test plate (Fig 5) consists of several sets of parallel lines ruled across a thin film of silver deposited upon a cover glass   The cover glass consists of a long narrow strip of glass worked optically plane on either side and in such a way that the strip tapers gradually in thickness from about 0 1 mm at one end to about 0 2 mm at the other end The cover glass with the film side down is permanently mounted on a microscope slide on which is engraved a scale indicating by increments of 0 01 mm. the thickness of the cover glass from one end to the other

The ruled lines are usually designated as the "white spaces" and the undisturbed silver film between adjacent ruled lines as the "black spaces " The silver film is not totally opaque but is sufficiently transparent to
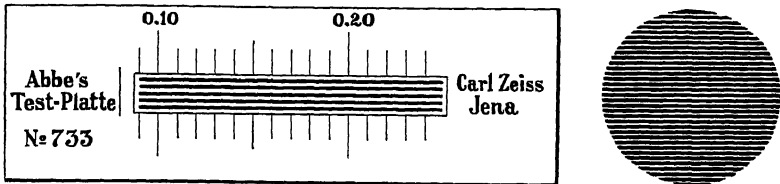
FIG 5 —ABBE TEST PLATE

reveal the silver grains   The ruled lines have jagged edges which form a delicate test object for high-power objectives

To test objectives, a microscope should be used which is fitted with the usual Abbe substage illuminating apparatus, so that a rapid transition from axial to oblique illumination can be made

The quality of the image at the center of the field and the changes which occur when the illumination is changed from axial to oblique are carefully observed   The performance of an objective is judged by the way in which the sharp edges of the rulings and the silver grains themselves are defined and also by the color and width of the color fringes which border the edges of the black spaces

Fig 6 illustrates diagrammatically the appearance of color fringes as seen with a test plate and a semi-apochromatic objective when using axial light   If the objective is pushed within the focus, the edges of the black spaces appear violet and if the objective is drawn without the focus, the color fringes change to apple green   This is known as symmetrical coloring because both edges of the black spaces are colored the same

The reasons for these color fringes are made clear by Fig 7, which illustrates in an exaggerated way the formation of the images with a semi-apochromatic objective when using white light and axial illumination of the test plate   In this diagram, the colors are shown separately instead of blended

When the objective is lowered, the yellow-green fringe first appears and then if the objective is lowered still further, the orange-blue and the red-violet combinations successively appear   It is evident that if the objective is pushed within the focus, blue-violet fringes should appear bordering the black spaces of the test plate or if the objective is pulled without the focus, the fringes should appear yellow-green

When oblique light is used with the test plate and a semi-apochromatic objective, the upper borders of the black spaces are fringed with apple-green color and the lower borders with violet, as illustrated diagrammatically in Fig 8   If the light is directed from a diametrically opposite direction, the order of colors will be reversed, the apple green appearing where formerly the violet appeared and vice versa   The same color arrangement persists regardless of whether the objective is pushed within or pulled without the focus   The coloring is now termed nonsymmetrical because the edges are not colored the same

The reasons for this nonsymmetrical coloring with oblique light are illustrated in Fig 9.   Light enters from the lower third of the substage condenser and illuminates the white space of the test plate a^1-a^2 At A_1 the image is really in the apple green but unless very closely observed this color is lost because of the brilliancy of the white space   The orange-blue (omitted to simplify the diagram) and the blue-violet appear as passing through the black space and have been so represented in the diagram   At A^2 just the opposite conditions obtain   The orange-blue and the blue-violet are lost and the yellow-green appears to come through the black space.   No matter whether the objective is raised or lowered, the same color relationship persists.

Cleaning Objectives and Oculars

It is important that one should know how to clean and care for microscope objectives   Objectives must be clean if they are to perform at their best.

When through using an immersion objective, the immersion fluid should be wiped from the front lens with a fresh piece of lens paper moistened with pure benzine   It may be necessary to use several pieces of lens paper, repeating the operation until the lens and its mount are clean, bright and dry.   The objective should then be stored in its case, away from the dust and smoke of the atmosphere   When handling objectives, the fingers should be confined to the knurled collar and they should not come in contact with the front and back lenses

To care properly for objectives and oculars the simple appliances shown in Fig 10 will be useful   A supply of very clean fine grade absorbent cotton should be stored dust free in a covered glass vessel.   Tufts of this cotton are twisted securely about the ends of wooden applicators   Care should be exercised to see that the end of the stick is deeply buried in the

OBJECTIVE
WITHIN
FOCUS

OBJECTIVE
WITHOUT
FOCUS

FIGURE 6

WHITE LIGHT

WHITE LIGHT

FIGURE 7

WHETHER THE OBJECTIVE IS
WITHIN OR WITHOUT THE
FOCUS THE COLORING
REMAINS THE SAME

FIGURE 8

A^1

a^1

a^2

A^2
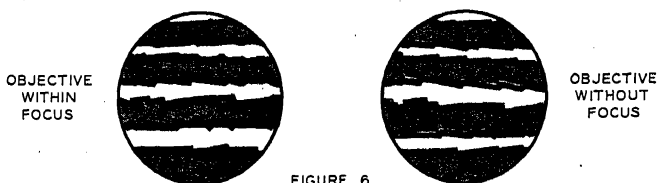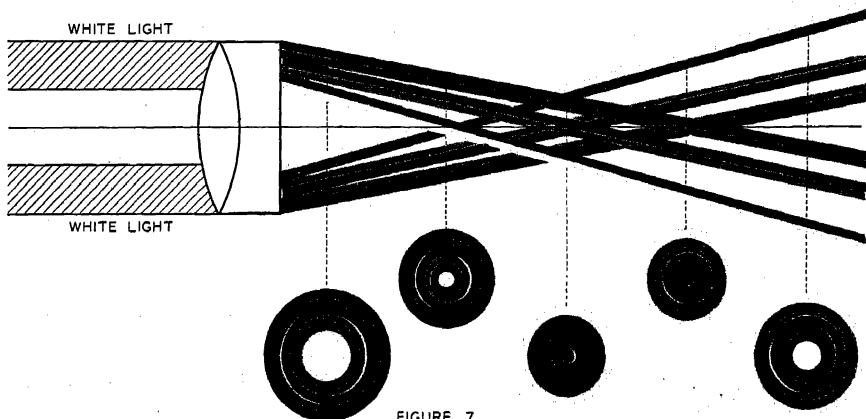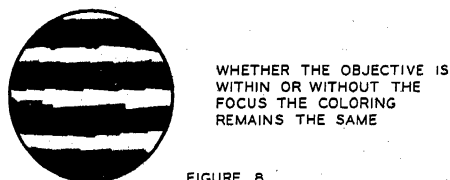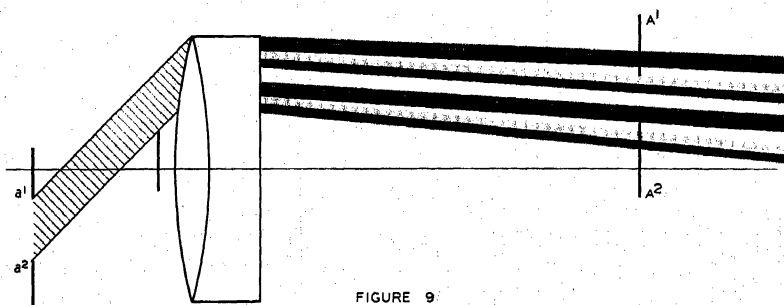
FIGURE 9

Fig. 6.—Color fringes seen with test plate and a semi-apochromatic objective when using axial light. Coloring is symmetrical.

Fig. 7.—Diagram illustrating the formation of color fringes using test plate and axial light. Colors shown separately instead of blended.

Fig. 8.—Color fringes seen with test plate and a semi-apochromatic objective when using oblique light. Coloring is nonsymmetrical.

Fig. 9.—Diagram illustrating the formation of color fringes using test plate and oblique light. Colors shown separately instead of blended.

cotton. This cotton swab is then moistened in benzine and the lens surfaces gently and carefully wiped. Several different swabs should be used in succession, especially if any immersion fluid has dried on the lens mounts or surfaces. All of this must be removed. The lens surfaces are
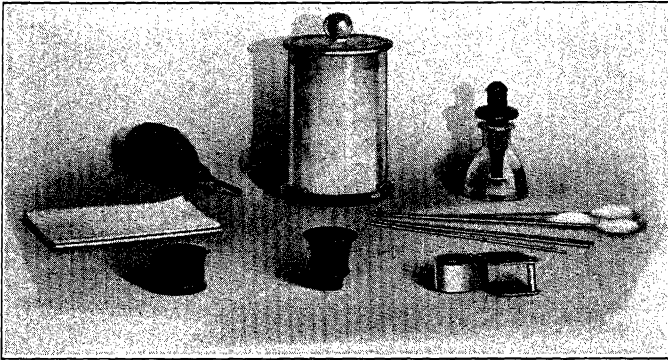
FIG. 10.—APPLIANCES FOR CLEANING OBJECTIVES AND OCULARS.

inspected with magnifiers. Finally the small hand syringe is used to blow loose dust particles and cotton linters from the lens surfaces.

Zeiss-Martens Metallurgical Equipment

The Zeiss-Martens metallurgical outfit is illustrated in Fig. 11. This is the equipment I have used for high-power metallography. It consists of an optical bench carrying an automatic arc lamp; a condensing system or illuminating train including cooling cells and the Martens type microscope. Aligned with the optical axis of the microscope is a large camera of 155 cm. bellows extension. The camera is mounted on rollers so that it may be moved backward, thus the operator may make visual observations. When ready to photograph, the camera is pushed forward on its stand and a light tight fit secured with the microscope by means of adapting collars, one slipped over the front board of the camera.

In our laboratory in New York City, street disturbances are troublesome and are transmitted to the steel framework of the building. To overcome these disturbances, a very solid and heavy maple platform has been provided. This platform rests on air cushions, consisting of rubber bags in canvas casings. This is as convenient a way as any to overcome vibratory disturbances in this particular type of equipment. The method has the disadvantage of raising the equipment about 8 in. higher than normal and the platform is somewhat inconvenient to work around. It does eliminate vibration troubles, which is a great deal in its favor.
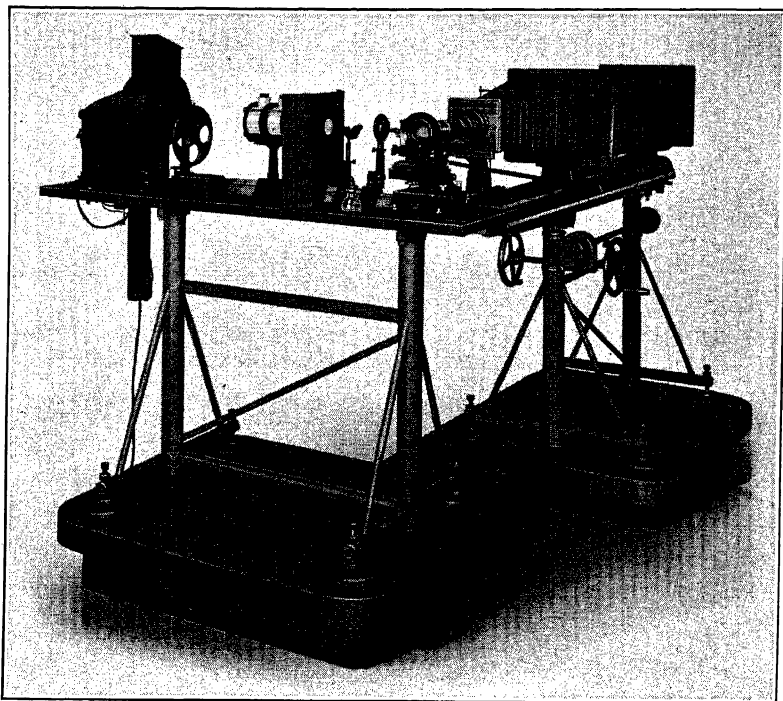
FIG. 11.—ZEISS-MARTENS METALLURGICAL OUTFIT.
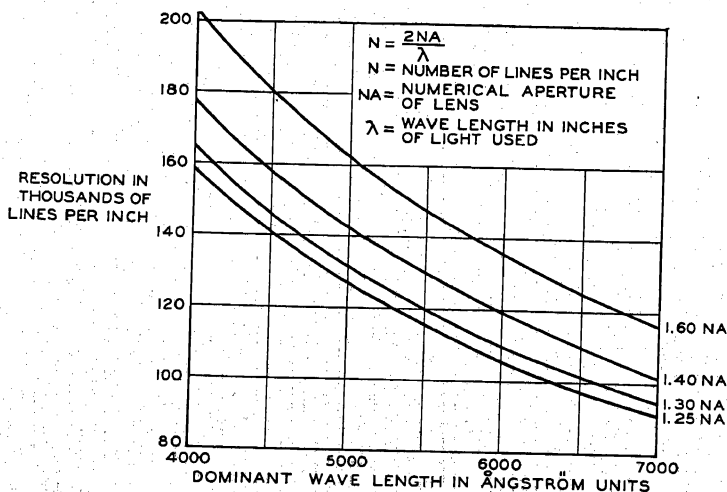
FIG. 12.—RELATIONSHIP OF THEORETICAL RESOLVING POWER; NUMERICAL APERTURE, AND DOMINANT WAVE LENGTH OF LIGHT.

Light, Color and Resolution

The resolution of a given apochromatic objective increases as the wave length of the light is decreased   Resolving power is usually expressed in lines per inch and is defined numerically by the Abbe equation

$$N = \frac{2NA}{\lambda}$$

in which N is the number of lines per inch, NA is the numerical aperture of the objective and λ is the wave length of the light expressed in inches

The relationship of theoretical resolving power, numerical aperture and dominant wave length of light is shown graphically in Fig 12   When the dominant wave length of the light is 4500 Ångstrom units, the apochromatic objective of NA 1 30 has a theoretical resolving power of about 146,000 lines per inch   The apochromat of NA 1 40 has a theoretical resolving power of 158,000 lines per inch for the same dominant wave length   This is a gain of only 15 per cent, nevertheless it represents a real achievement in optical performance   It is true that the personal errors may be such as to mitigate entirely this gain in resolving power or actually to result in a better picture with the objective of NA 1 30 than with the objective of NA 1 40   A much higher order of skill is required to use the higher aperture objectives

The equation expressing theoretical resolving power is based on the assumption that the detail being resolved consists of equally spaced lines—in other words, a very fine ruling or grating

Metallographic specimens do not consist of rulings but usually their structure exhibits the greatest variation in detail and in contrast   The microscope, then, is not dealing with a ruling but under the conditions its performance must be more along the lines of the ultra-microscope   It is possible to photograph in metal specimens minute details of structure because these details are actually single particles or lines disposed in a field of maximum contrast   If there were a succession of these details all aligned side by side and equally spaced, the indications are that performance of objectives would follow Abbe's formula.

We see objects by the light which they reflect   If differently colored objects lie side by side and are viewed by light of different colors, marked differences in contrast can be developed by the simple expedient of varying the color of the light by which we view the objects   This is due to the fact that selective absorption of certain wave lengths in the light is taking place   An object appears red, for example, because it is absorbing the green and the blue rays of white light and reflecting the red rays

A black button on a piece of black velvet is not a conspicuous object but a white button is very conspicuous   It is conspicuous because of the contrast which is developed   The black velvet absorbs most of the light which falls upon it whereas the white button reflects most of the light, hence there is maximum contrast.
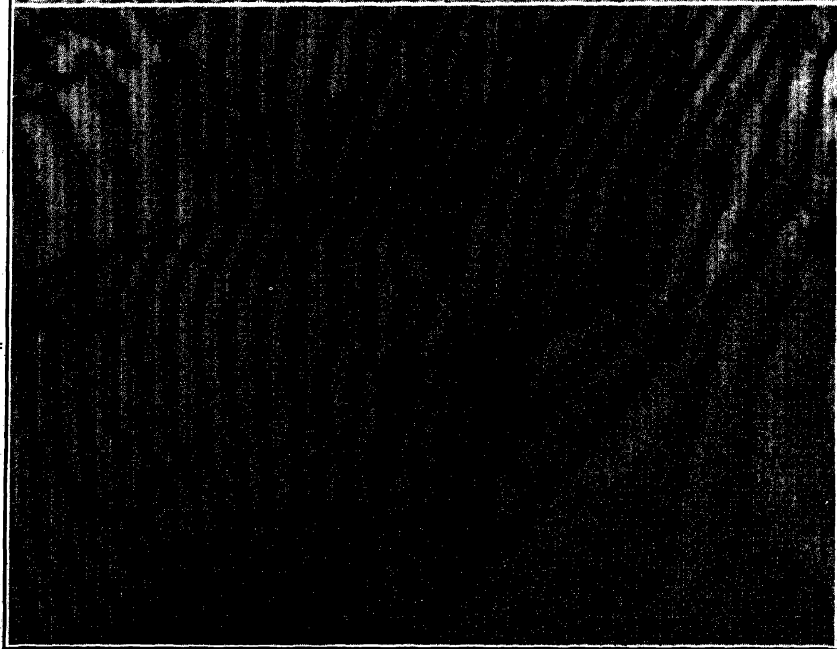
Fig. 13.—Pearlite taken with yellow-green light.   × 3300.
Fig. 14.—Same field as in Fig. 13, taken with blue light.   × 3300.
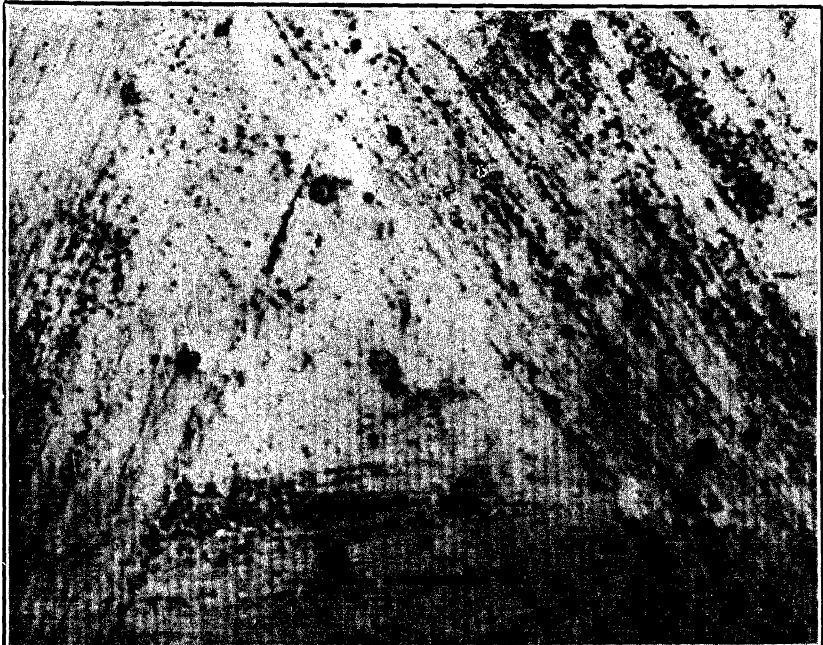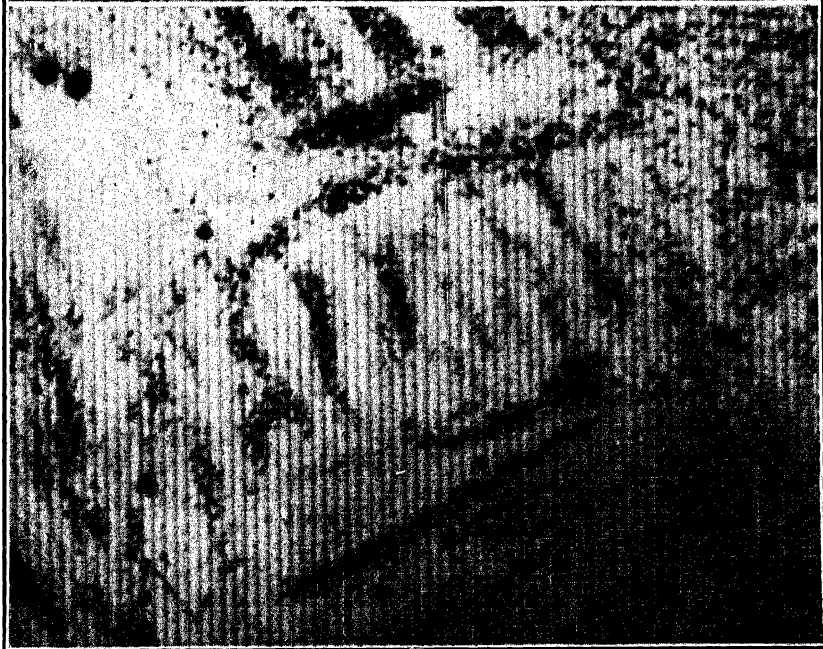
FIG. 15.—DUCTILE MARTENSITE. APOCHROMATIC OBJECTIVE OF NA 1.30. × 3500.
FIG. 16.—DUCTILE MARTENSITE. APOCHROMATIC OBJECTIVE OF NA 1.40. × 3500.
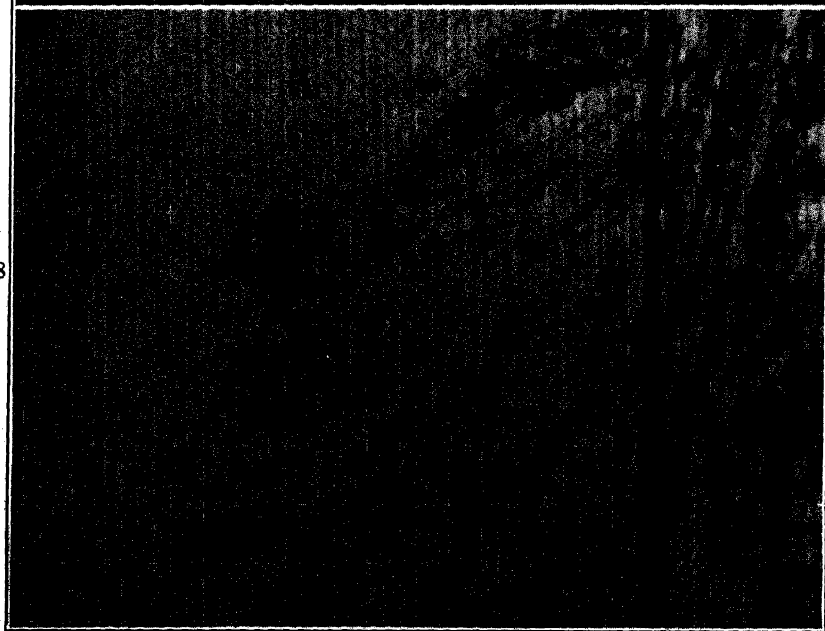
FIG. 17.—DUCTILE WHITE MARTENSITE, THE SOLID SOLUTION STATE. MONO-BROM-NAPHTHALENE OBJECTIVE OF NA 1.60. ×3500.
FIG. 18.—TOOL STEEL HEATED TO A HIGH TEMPERATURE AND QUENCHED. ×3500.

It is fortunate that in metallography the color of light which develops maximum resolution is also the color of light which generally develops greatest contrast. In iron and steel specimens, details of structure in many cases develop in shades of brown as the etching proceeds The matrix or background is much lighter in color, or even white To accentuate contrast, a blue filter should be used and as the blue region of the spectrum comprises the shortest wave lengths, resolution is also promoted

If contrast is not developed in a specimen, certain details of structure may be lost entirely or only faintly revealed in the photograph I can illustrate this point by photographs of pearlite Fig 13 was taken with yellow-green light and Fig 14 is the same field photographed with blue light The carbide plates are very faintly brought out with red or yellow-green light but they are well developed with the blue light

In Figs. 15, 16 and 17 I have compared the performance of the apochromatic objectives of NA 1 30 and NA 1 40 and the mono-brom-napthalene objective of NA 1 60 The photographs are instructive not only because of what they show concerning the differences in resolving ability of the objectives but also because of what they teach about the phenomena of the hardening of steel

The specimen is a low-carbon steel, about 0.10 per cent carbon, which has been heated to a very high temperature and quenched in a large stream of water I am indebted to Mr R H Smith, who prepared the specimen by the special heat-treating process which he has described in the literature.[1] The heat treatment has produced a condition which has been described as "ductile martensite "

Apparently the austenitic grains have been transformed to grains of ferrite containing the carbide in solid solution or highly dispersed. In the photographs, we see evidences of decomposition The grains are a straw yellow color as seen through the microscope and they are surrounded by a network of ferrite which is white Crystallographic planes are developed by the formation of dark particles, probably of the nature of troostite and in this specimen the evidences of needlelike figures are seen It is this structure, more highly developed in steels of higher carbon content, that characterizes martensite.

Some 10 years ago, when the early steps were being taken in the development of high-power metallography, the microscope was generally regarded as an instrument of science which had yielded its basic store of knowledge It had become a utility instrument, but as a matter of fact, photomicrographs appearing in the literature failed to show an astounding order of resolution Opinion held that the limit of achievement had been reached; technique had reached its zenith; new tools were needed I

[1] R H Smith Some Physical Properties of Low Carbon Steel *Trans* Amer Soc Steel Treat (1925) **7,** 569

quote from a publication of the period which perhaps expresses a point of view then current.

"The microscope had done its best for us but the smallest thing which it could show us was composed of billions of atoms   No improvement could be made in lenses· technique had reached its highest   The difficulty was really due to the fact that light is a wave motion and light waves cannot show us the details of objects unless the objects are much larger in every way than the length of the wave "[2]

I have not a well defined notion of what the ultimate limit of resolution may be   I am sure that it has not been reached as yet because with the same optical parts I am now able to resolve details of structure which a few years ago were a closed book to me   Technique certainly has not reached its highest development and better microscope lenses are being made available

There will shortly be delivered in New York a new metallographic equipment on which we have been cooperating with the Zeiss scientific staff   I have recently put it through its paces in Jena and I speak with a measure of assurance when I say that we shall see some revolutionary advances in the art of metallography   We shall be able to achieve crisp brilliant images at twice present limits, the order of resolution will be improved, and we shall have better optical and mechanical means at our disposal

Metallographers deal with plane surfaces and with linear distances Details of structure have length and breadth   They may be so many atom diameters or so many other units wide or long   It is distances and areas with which the metallographer concerns himself—not volumes or masses   What he wishes to know is the diameter of the particle or its length and breadth, and by evaluating enough particles he will arrive at the approximate shapes and sizes of the particles.   He can plot a uniformity curve and show how the particles occur and vary

A minute detail of structure when photographed with red light appears slightly larger and not so well defined as when photographed with blue light and details are rendered still smaller when photographed with ultra-violet light   As the wave length of the light decreases, the apparent size of the particle decreases   Thus it appears probable that the actual particle size is smaller than the photograph shows it to be

That we can obtain real images of details which measure but a few hundred atom diameters across will be clear from some of the photographs which follow   We also shall see, clearly defined, details of structure which by actual measurements are only a fraction of the wave length of the light used

In the preparation of metallographic specimens, our object is to produce a highly polished plane surface free from alterations, so that the

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[2] W H Bragg Concerning the Nature of Things   New York, 1925   Harper

details of structure developed by etching will be typical of the metal as a whole   Our aim is not always fully achieved but, in most cases, I believe that we have accomplished a very close approximation

To illustrate some of the ideas I have expressed, I shall show some typical structures and I shall give the views which I hold on the interpretation of the results   They may or may not be correct but to me they seem the most logical and the most plausible   In my experience delving into the structure of matter, it has always struck me that nature does not take a roundabout course to accomplish a given result   Natural processes seem to follow the straight line—the shortest distance between two points.

In the study of metals, I see a certain regularity and orderliness—a sequence of events wherein one deals with allotropy; with solid solutions; with aggregates, with volume changes, with temperature changes, with stable and unstable conditions; with particle sizes which harden the matrix, with particle sizes which soften the matrix; but there seems always to be present in an alloy that inherent tendency to arrive at a condition that is stable for the prevailing temperature condition

If a specimen of tool steel is heated to a high temperature and quenched, we find the structure after careful preparation to consist of white needlelike forms which are more resistant to the etching reagent than the fillings between (Fig 18)   So far as microscopic vision is concerned, these white needlelike forms appear to be solid solutions but the state of this solid solution is unstable because decomposition sets in when the temperature is raised to 100° C for a few minutes [3]   Both white and dark areas are very slowly attacked by the reagent but the fillings develop first   The specimen is magnetic and other investigators have concluded that only a small proportion of gamma iron can be present in a specimen of this kind

Here and there throughout the specimen, individual needle forms appear mottled or have a striated structure indicating that such areas are aggregates—something has precipitated from the solid solution state (Fig 19)   We may even find needle forms which show the transition taking place (Fig 20)

If the specimen is etched with sodium picrate, it darkens readily, indicating the presence of carbide   Evidently one thing that takes place is the appearance of carbide   All needle forms darken with sodium picrate but this reagent is used boiling so that any interpretation based on its use must take into account the fact that the specimen has been tempered at 100° C   It is no longer in the "as quenched" condition

When a "white martensite" specimen is tempered, for example as by grinding its surface to prepare for metallographic examination, the needle forms are darkened and appear not white but a golden yellow   Obvi-

[3] F F Lucas Further Observations on the Microstructure of Martensite   *Trans.* Amer Soc Steel Treat (1929) **15**, 339
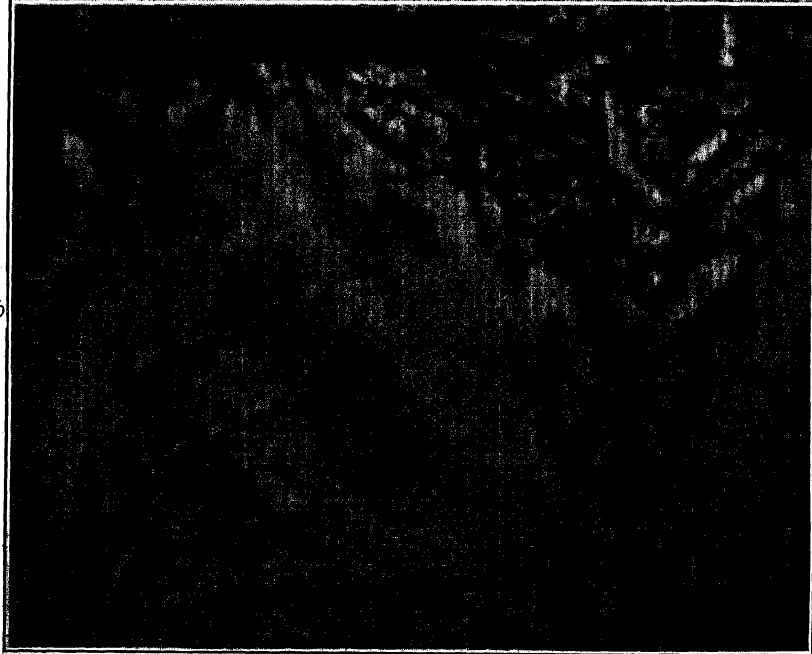
FIG. 19.—PRECIPITATIONS FROM SOLID SOLUTION STATE OF SPECIMEN OF FIG. 18.
× 3500.

19c

20
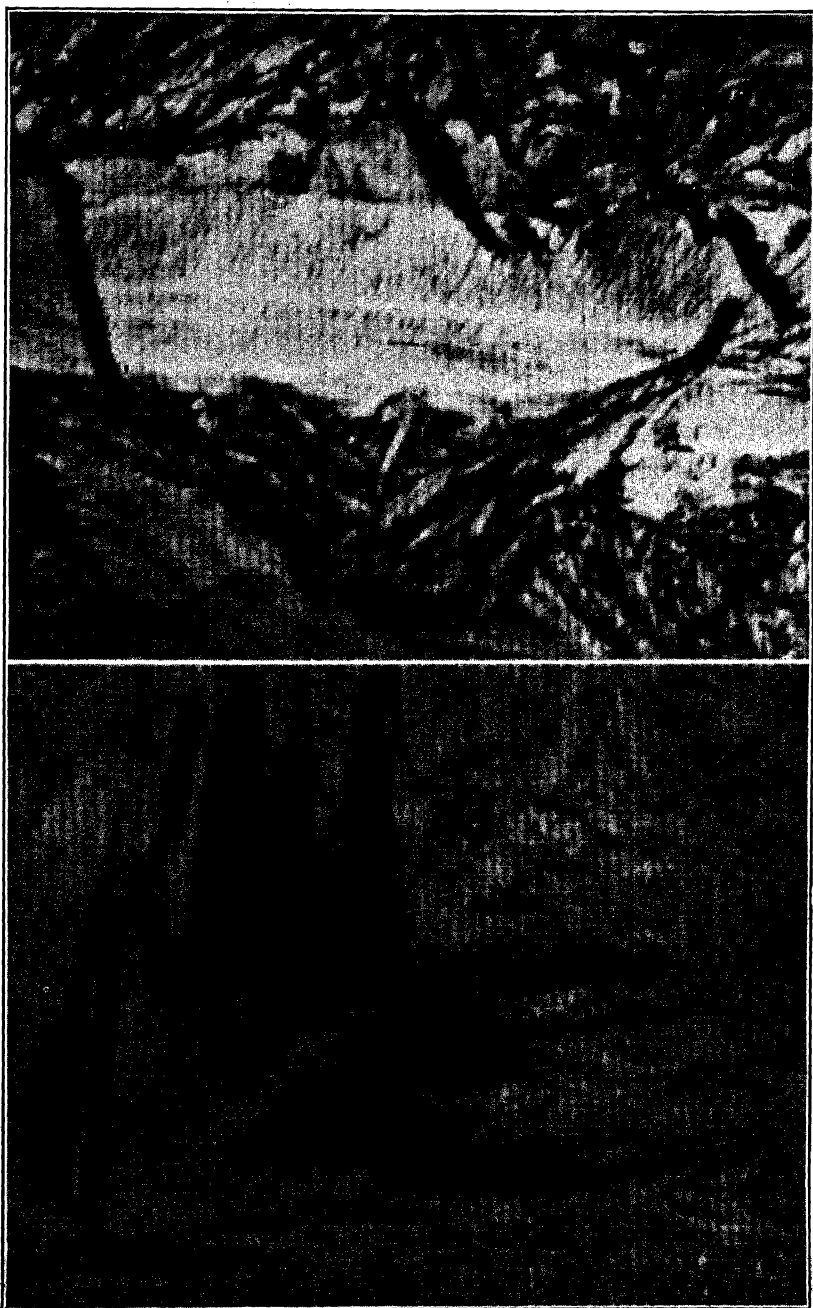
Fig. 20.—Needle forms showing transition taking place in specimen of Fig. 18. × 3500.
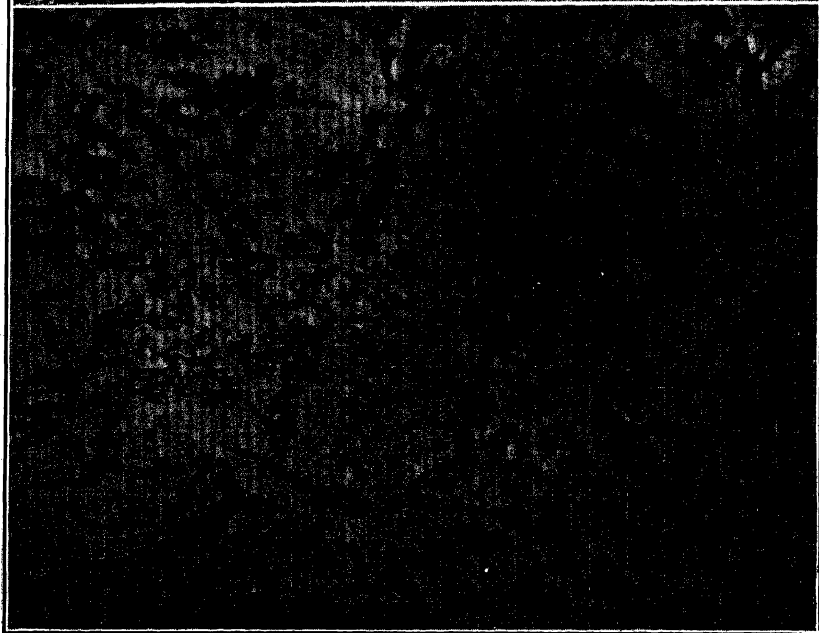
FIG. 21.—DARK NEEDLE FORMS IN WHITE MARTENSITE DUE TO TEMPERING BY GRIND-
ING.   × 3500.
FIG. 22.—NEEDLE FORMS MARKED BY CARBIDES IN FERRITE MATRIX.   × 3500.

ously a precipitation of some sort has occurred at the surface, due to tempering in the grinding operation (Fig 21)

If these "white martensite" specimens are tempered by increments of 100° C to a temperature just below the critical, progressive softening takes place and we may follow the structural changes   Just below the critical, the specimen has a hardness of about C-28 on the Rockwell scale   The structure consists of needlelike forms in a ferrite matrix (Fig 22)   Where the old needle forms were present in the hardened state of the metal, we now find their outlines marked by carbides   At first, these carbides appear as a flocculent mass which is on the verge of resolution   As tempering continues, the particles grow larger and may be seen as individuals when the drawing temperature becomes about 400° C

These photographs were taken about four years ago   More recent work shows a higher order of resolution

Fig 23 is a photograph of ductile martensite, carbon about 0 10 per cent, in which is shown the ferrite grain boundary network enclosing grains in process of decomposition   These grains are straw yellow in color and the grain boundaries are white, indicating difference in composition between the boundary areas and the interior of the grains The small black particles by measurement of the photographs are about 300 atom diameters across, dimensions are based on the alpha iron atom The mottled areas indicate the presence of a particle size beyond the ability of the lens to resolve   We are unable to see the individual particles because of their small size and their close proximity.   They appear as a cloud or flocculate

The next five figures illustrate martensitic structures in a specimen of plain carbon tool steel (Figs 24, 25, 26, 27 and 28)   The needle forms are either white or mottled   The mottling indicates decomposition   the carbide particles have commenced to appear   The particle size is very much less than 300 atom diameters   It represents tempering or softening—not great hardness   The particle size of dispersed carbide accountable for maximum hardening must be very small indeed

The dark lines are very small quenching cracks   They are confined to the needle areas   Generally speaking, the small cracks run across the needles, but some run along the edges of needles or lengthwise of the needles   The cracks do not seem to occur in the fillings and this would suggest that the mode of decomposition as indicated by the fillings has been somewhat different   If the cracks represent strains set up in quenching due to the rapidity with which volume changes occurred, these cracks must indicate that transformation in the fillings has been at a slower rate and the metal has had time to adjust itself in these localities

The significance and the control by heat treatment of the development of these minute cracks seems to me to be of great practical impor-

FIG. 23.—FERRITE GRAIN BOUNDARY NETWORK IN DUCTILE MARTENSITE, ENCLOS-
ING GRAINS IN PROCESS OF DECOMPOSITION.   × 3500.
  FIG. 24.—MARTENSITIC STRUCTURES IN PLAIN CARBON TOOL STEEL.   × 3500.
Showing presence of minute quenching cracks.   The cracks are associated with the
                  needles—not the fillings between needles.
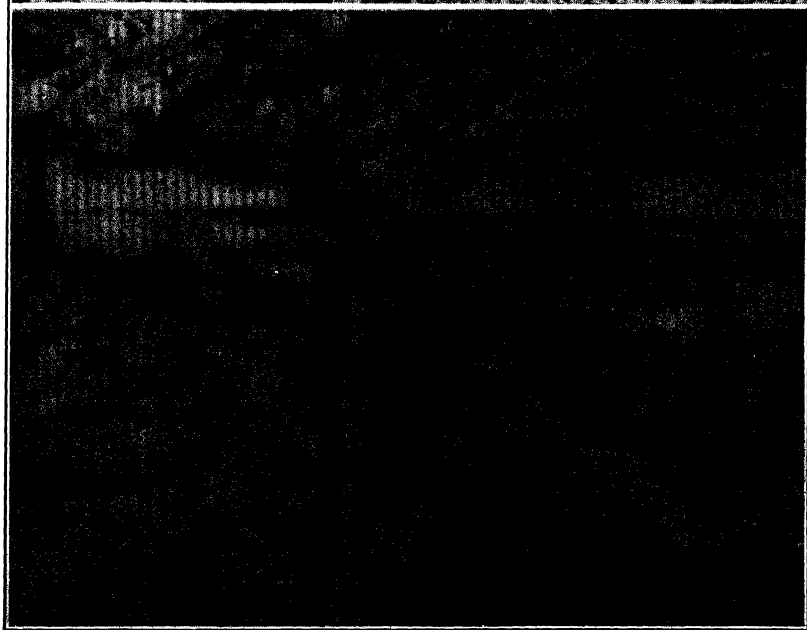
Fig. 25.—Martensitic structures in plain carbon steel. × 3500.
Fig. 26.—Martensitic structures in plain carbon steel. × 3500.
Showing presence of minute quenching cracks. The cracks are associated with the needles—not the fillings between the needles.
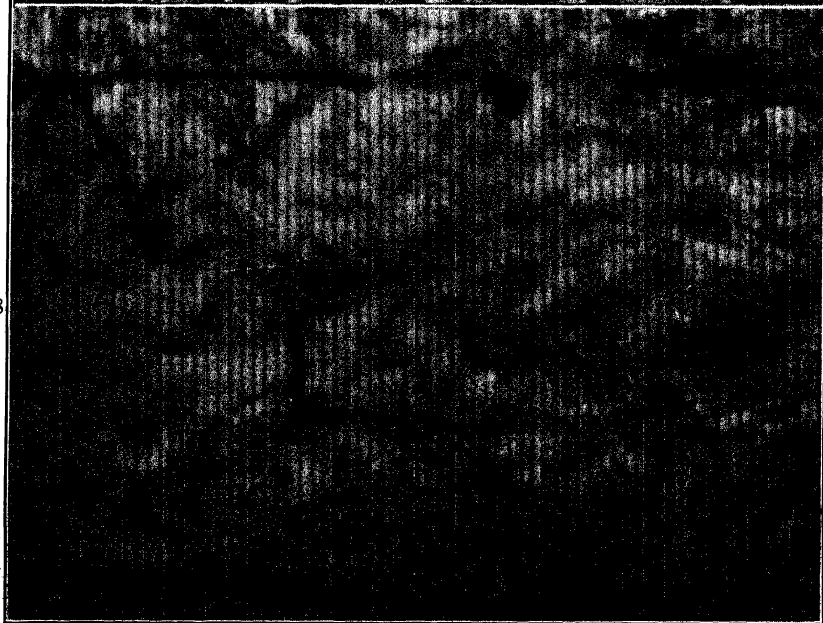
FIG. 27.—MARTENSITIC STRUCTURES IN PLAIN CARBON STEEL.   × 3500.
Showing presence of minute quenching cracks. The cracks are associated with the
needles—not the fillings between the needles.
FIG. 28.—MARTENSITIC STRUCTURES IN PLAIN CARBON STEEL.   × 3500.

FIG. 29.   FIG. 30.

FIG. 29.—FATIGUE CRACK IN ARMCO IRON LIGHTLY ETCHED. × 3500.
FIG. 30.—ACTUAL EXTENSION OF CRACK SHOWN IN FIG. 29. × 4800.

tance. If these are truly cracks and not lines of strain opened by the etching (and we shall soon see that they are cracks), it means that those who are concerned with the production of hardened steel parts have something else to think about   If a hardened steel part containing these minute cracks is one which will be subjected to reversed cycles of stress, each little crack becomes potentially the starting point for a fatigue failure

Two very able investigators, Davenport and Bain,[4] have recently published a significant piece of research in which they show us how we may control the transformations in steel by a deferred or two-stage method of quenching   Volume changes have an opportunity to adjust themselves and one might expect by the methods they describe to secure parts of great hardness, yet with freedom from these minute fissures and cracks   If so, it should be a boon to those who are concerned with the production of parts that must withstand reversed cycles of stress Surely the methods will bear further study and application

One of my associates at the Laboratories, J R Townsend, who for the past five years has devoted much time to fatigue studies, suggests that these very small cracks may fully account for the erratic behavior sometimes encountered in his tests of hardened steel specimens

It seems possible that these cracks might be lines of strain opened by the etching reagent   Some work a few years ago[5] revealed that a fatigue crack which apparently ended when the specimen was lightly etched (Fig 29) actually extended beyond that apparent ending to a large inclusion toward which it was trending (Fig 30)

The identical specimen that revealed the presence of the minute quenching cracks was strain-annealed for 2 hr at about 200° C   The surface was first carefully ground away to get well below any surface conditions developed by the previous etching   After annealing, the specimen was again prepared and etched   The cracks developed, as may be seen from Figs 31, 32, 33 and 34

Tempering at 200° C has caused fine carbides to precipitate and the entire structure now is mottled   Contrast has been diminished and the specimen is difficult to photograph   The particle size of the carbide and the close proximity of the particles in general is responsible probably for failure of the lens to resolve fully the details

It seems certain that the action of the etching reagent has caused the cracks to widen at the surface, so that any measurements we may make are bound to err.   The cracks develop by etching and only those which are relatively large can be seen in the unetched specimen   If we are to

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[4] E S Davenport and E C Bain Transformation of Austenite at Constant Subcritical Temperatures   *Trans* A I M E , Iron and Steel Div (1930) 117

[5] F F Lucas Observations on the Microstructure of the Path of Fatigue Failure in a Specimen of Armco Iron   *Trans* Amer Soc Steel Treat (1927) 11, 531
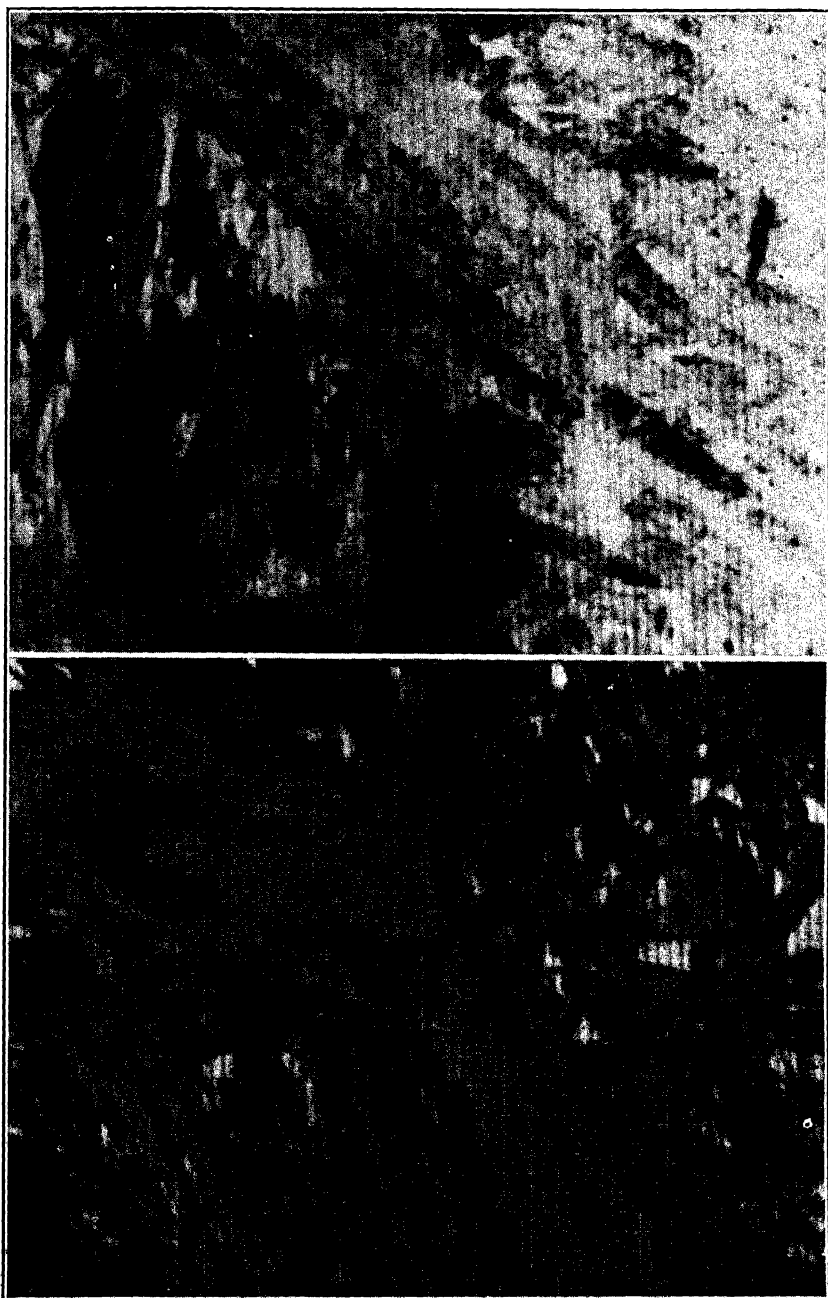
FIGS. 31 AND 32.—CRACKS PRESENT IN SPECIMEN OF FIG. 29 AFTER STRAIN-ANNEALING
OF SPECIMEN.   × 3500.
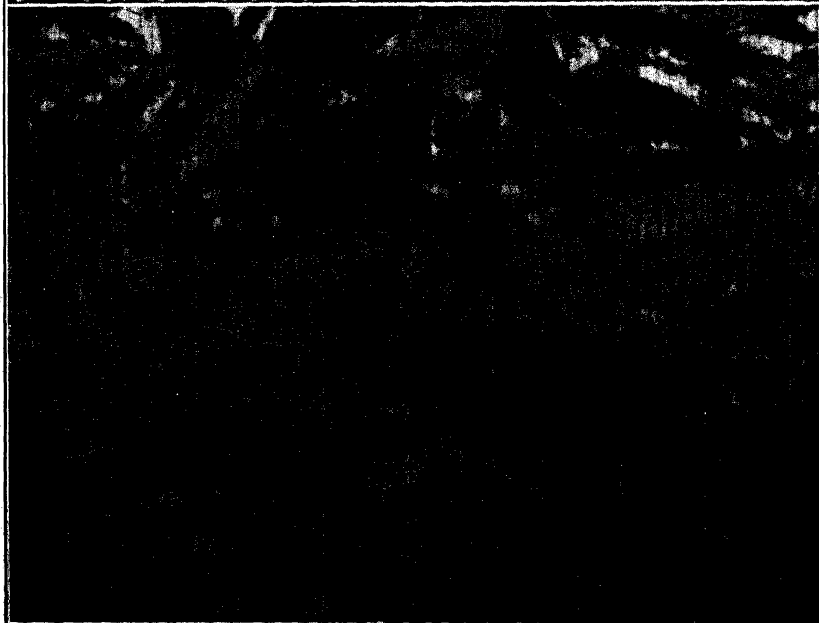
FIGS. 33 AND 34.—CRACKS PRESENT IN SPECIMEN OF FIG. 29 AFTER STRAIN-ANNEALING OF SPECIMEN.   × 3500.

arrive at some reasonable approximation of their dimensions, we must make allowances for probable enlargement.

The measured widths of the small cracks as revealed by the photographs at a magnification of 3500 ranges from about 0.01 to 0.04 in. and their length ranges upward from about 0.04 in. It is a simple matter to calculate the minimum dimensions. The width becomes 2.86×10^{-6} in. and the length becomes 11.44×10^{-6} inch.
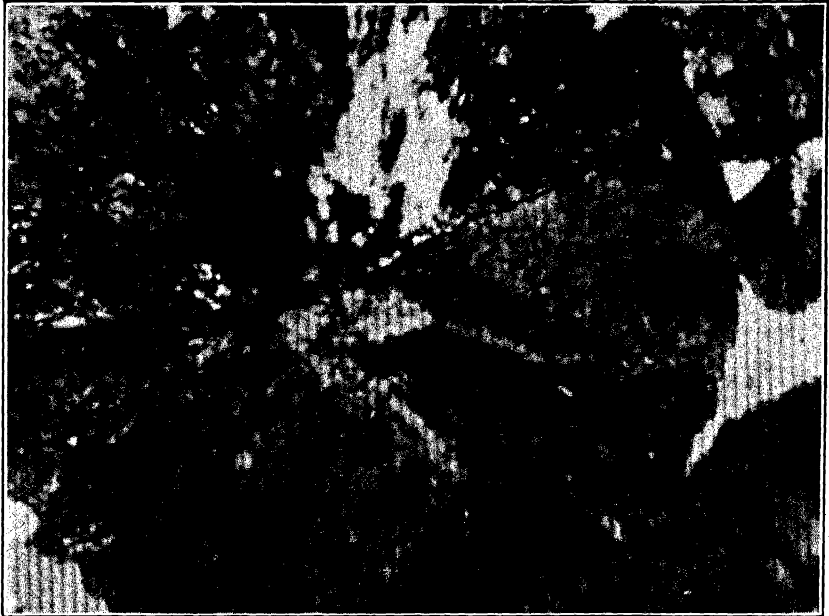
FIG. 35.—RADIAL GRAINS ABOUT A NUCLEUS OF GROWTH IN TROOSTITE.   × 3230.

The distance across the space occupied by the alpha iron atom is given as 2.86×10^{-8} cm., which converts into 1.13×10^{-8} in. If we divide the minimum measured width of crack by the dimension of the atom, we find that the probable minimum width of the cracks as measured on the photographs is of the order of 250 atom diameters and the minimum length becomes about of the order of 1000 atom diameters.

A conservative estimate of the crack enlargement in width is perhaps 10 times, and it may be much greater. Thus if we use the factor of 10, it is possible to have in plain carbon tool steel minute cracks which may be of the order of 25 atoms wide and 1000 atoms long. Doubtless they may be starting points for fatigue failures if the conditions are favorable.

If desired, we may convert dimensions into wave lengths or fractions of wave lengths. The dominant wave length of the light used was 4500 Å., which becomes by conversion 4.5×10^{-5} cm. or 1.77×10^{-5} in. and,

FIGS. 36 AND 37.—TROOSTITIC STRUCTURE. × 3500.

Figs. 38 and 39.—Troostitic structure. × 3500.

dividing the minimum width of the crack $2\,86 \times 10^{-6}$ by the wave length, we find the minimum width of crack to be of the order of $0\,16$ wave length The cracks, it will be remembered, are relatively large compared with some other details revealed in the photographs, so that a very much higher order of resolution than this has been achieved

Another constituent of hardened steel is troostite

In 1924, a paper was presented before the Franklin Institute[6] in which the nature of troostite was discussed. Fig 35, taken from that paper, shows a nodule of troostite to consist of radial grains about a nucleus of growth. Detail of the grains seems beyond the power of the lens Improvements in technique have since enabled us to break up these troostitic structures[7] They are very fine pearlite Figs 36, 37 and 38 are representative of the structure

When a hardened steel specimen contains the needle forms of martensite and the nodules of troostite, the minute quenching cracks are confined to the needles Specimens whose structure is all of troostite such as is shown in Fig 39 seem to be free of all evidences of cracks

On Dec 29, 1916, a joint meeting of the Section of Engineering of the American Association for the Advancement of Science was held with the four Engineering Societies[8] Professor Howe was chairman of the Section of Engineering and in his introductory address on the Relation between Engineering and Science, he spoke of the structure of matter in the following words

"We begin to get a glimmering of the vastness of the scheme of creation when we remember that every lengthening of man's artificial vision by means of telescope and camera, every new strengthening of telescope, sensitizing of plate, and lengthening of exposure brings a proportional increase in the number of visible suns, telling us that even at that inconceivable distance we have not begun to approach the limit of the discoverable universe When we turn from telescope to microscope and then to the inferred constitution of matter, we find with every new refinement of observation and inference a proportional addition of new wonders, a proportional increment in the complexity of natural phenomena "

And thus we bring to conclusion this eighth Howe Memorial Lecture

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[6] F F Lucas High-power Metallography—Some Recent Developments in Photomicrography and Metallurgical Research *Jnl Franklin Inst* (1926) **201,** 177

[7] F F Lucas Structure and Nature of Troostite *Bell System Tech Jnl* (1930) **9,** 101

[8] H M Howe Relation Between Engineering and Science *Science* (1917) **45,** 273.

Beneficiation of Iron Ore

By Clyde E Williams,* Columbus, Ohio

Abstract†

Estimates indicate a life of known Lake Superior iron ore reserves of 20 to 30 years   Although some believe the future ore supply will come from foreign sources and will be brought to interior points via the projected Great Lakes-St Lawrence waterway, and others fear a displacement of the interior steel-producing districts to the Atlantic seaboard, the author has faith that American engineering skill will make possible the use of lean ores from the Lake Superior district

Three general types of Lake Superior ores and ore formations, that represent possible reserves and require beneficiation, are (1) the wash ores of the western Mesabi range, (2) the partly leached hematitic formations, and (3) the oxidized but largely unleached iron formations The total tonnage represented by (1) and (2) is not large, but the recovery of iron from present washery tailings would bring on the market the equivalent of nearly one million tons of wash ore, annually   Group 3 comprises the magnetic iron formation of the eastern Mesabi range, the hematitic formations including the taconites of the Mesabi range, and the iron formations of all the other ranges   These formations represent our future supply of iron ore   Their treatment requires intensive research because the bulk of the iron oxide and silica minerals exist in a finely disseminated condition   The possibilities of the adaptation of tables, oil flotation, and other processes warrant extensive study Cheaper method of agglomeration of the concentrate is essential

Recent developments in better preparation and sizing of blast-furnace charges indicate that substitution of agglomerated ore for fines will increase furnace efficiency and output   If agglomerated beneficiated ore can be shown to rate a per-unit premium for iron contents over the base rate or a premium for structure, the payment of these would greatly assist in enlarging our iron ore supply   Since present methods of taxation of ore reserves, which encourage the rapid depletion of rich ores, will result in using up our rich ores and later on putting domestic producers at a disadvantage in competing with foreign producers, it would seem highly provident to conserve our rich ores and to increase the use of beneficiated ores as soon as possible

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Round Table

(C B Murray presiding)

C B MURRAY, Cleveland, Ohio —We have brought up this round table conference for two principal reasons (1) to get the producers and consumers better acquainted with one another, (2) to discuss some of the problems both have in attempting to meet the views of the other group We hope that these problems will be discussed in all fairness

We all admit that, at present, the beneficiation of ore, coal and limestone must necessarily add something to the cost of these products over and above the cost of the raw materials It would seem, however, that a discussion of how such beneficiation would or would not benefit the user might be in order irrespective of other considerations It is for such a discussion that this conference was called

Mr Williams' paper has in a general way expressed the ideas in beneficiation and has brought up several questions which might be well worth considering One of the questions is this What are the advantages and disadvantages of the three methods of agglomeration, sintering, nodulizing and briquetting? Mr Harrison, will you not tell us something about sintering?

IRON-ORE SINTER

P G HARRISON, Ironton, Minn —A sinter properly burned from a soft ore on the Mesabi or Cuyuna range can be made so that when dumped into a car and then dumped into dock, and then from the docks dumped into a boat and unloaded at lower lake ports, it will have a screen test showing about 0 75 per cent through 100 mesh Handling beyond that point, so far as I know, does not break the sinter down any material amount With the sinters which we ship, about 30 to 35 per cent will be coarser than 1-in mesh, the other sizes ranging between these figures However, the important thing is that only about 0 75 per cent goes through 100 mesh The advantage of sinter in the blast furnace, to my mind, is entirely due to opening up of the charge I do not believe sinter is any more easily reduced than iron ore, but it is more easily reduced than fine iron ore, because fine iron ore blocks up the furnace That is merely my opinion I believe Mr Joseph and some others have done a great deal of work on that particular phase of the subject Sinters should do the same thing that an old-range lumpy ore does towards opening up the furnace for the use of a fine Mesabi ore, and it is used that way in some of the sinters which we ship

D J DEMOREST, Columbus, Ohio —What kind of sintering machine does Mr Harrison refer to, and how deep a bed is used?

P G HARRISON —We use a Dwight-Lloyd machine and an 18-in bed The depth of bed is proportionate to the amount of pore space there is in the ore If you have a coarse material, you could probably go to an indefinite depth The principle is just the same as in the blast furnace where you must have a high blast pressure in order to get through fine material, but only a low pressure for coarse ore We do not have the pressure, but we do have a vacuum As long as we can pull air through the bed, we can keep it burning We have had bed through which we could not pull air, and had to cut the sinter bed to about 11 in deep Our normal is an 18-in bed

MEMBER —What additional fuel do you use in the bed?

P G HARRISON —We have to use about 11 per cent additional fuel, because there is none in the ore In sintering a crude ore, you have to put in all of the fuel

MEMBER —You do that in the bed? You do not use oil?

P G HARRISON —No We mix a stream of coke breeze and ore in a pug mill and put it on the bed and ignite it with a gas flame produced from the distillation of a distillate

MEMBER —What is the composition of the exhaust gas?

P G HARRISON —It is put through a wet dust collector and then exhausted to air out of a stack The composition is very largely moisture We drive out about 25 per cent of the total weight of ore put upon the bed That drop in bulk is almost entirely in free or combined water In our ore and also the ores of the International Harvester, the moisture will run between 14 and 20 per cent, and the loss in ignition between 5 and 13 per cent Our average is 25 per cent loss Sagmore ore is approximately 30 per cent

MEMBER —What happens to the carbon?

P G HARRISON —It goes up through the stack I have never taken a gas analysis I do not know whether there is a considerable portion of CO Of course, we do produce a magnetic material, and that implies that there is an excess, or at least that there is considerable CO in the bed Otherwise we would not get a magnetic sinter, we would get a hematite sinter, which would not be sinter at all, but dust

D J DEMOREST —Do you know how much ferrous oxide there is in the sinter?

P G HARRISON —No, I do not I think it is very slight Analyses have been made of our sinter and it is almost entirely magnetite or ferrosilicate

T L JOSEPH, Minneapolis, Minn —I believe sinter contains about 15 per cent ferrous iron, probably as magnetite

P G HARRISON —The iron is largely in the form of Fe_3O_4 The only analysis we take regularly on that is the gain on ignition Ordinarily when we deal in iron ores, we obtain loss on ignition, because if ore is raised above 212° F to the point where the chemical water is decomposed there is a loss of weight, i e, loss on ignition In our case if dry powdered sinter is heated it burns slowly and oxidizes from Fe_3O_4 to Fe_2O_3, and the gain on ignition ordinarily ends at 1 33 per cent, which represents gain in oxygen weight

MEMBER —Would you mind stating what your preparation is, whether your ore is screened in a natural state or washed?

P G HARRISON —Almost all the ore we use is sent to the plant direct without any preliminary treatment There it is crushed roughly to 4 in and then screened through ⅜ If we screen to a coarser size we find a tendency towards sinter particles which have a core of unsintered material The fines are then sintered At times the coarse is shipped direct to the docks and at other times the coarse ore is reduced by crushing and the entire material is sintered

The fine material after being screened is stored in stock bins The stock bins may have ore of different analyses, so we are able to join different mixes of material to obtain the analysis which we are shipping at that particular time We have other stock bins containing coke breeze These two materials are dumped on the same traveling belt, elevated and mixed with water It is a peculiar thing, no matter how much natural moisture the ore may have, some water must be added to make a sinter stay together

MEMBER —You have no drying preparatory to sintering?

P G HARRISON —The only drying we have is by action of the return sinter We screen all sinter over 1¼-in grizzlies The fines, which are red hot, fall back on the same belt with the ore going into the plant There is a considerable drying there The average moisture of ore after such drying is from 12 to 14 per cent in most of the determinations we have had made Then we raise the moisture to 13 to 15 per cent with some additional water added in pugging Again, for some reason or other, it is necessary to add some additional moisture in the pug mills just before sintering, or the material will not ignite

L E IVES, Cleveland, Ohio —Mr Harrison mentioned the fact that in his opinion sinter, because it is sinter, is no more easily reducible than iron ore I think there has been a prevailing opinion that it has been more easily reduced, because its open cellular structure offers greater area to the gases

P G HARRISON —Perhaps I should qualify that I think if you take an individual particle of sinter broken down to a size where there is not a considerable amount of air space, that individual particle will not reduce any more easily than a piece of lump ore But an aggregate of sinter, or an aggregate of sinter and coarse ore, should reduce vastly more easily than a fine ore material that cannot be reached by the gases The easy reducibility of sinter in the blast furnace is not because of the character of individual particles, but because of the structure of the aggregate

MEMBER —You say the sinter is a magnetite The ore is not an actual magnetite?

P G HARRISON —No The ore has an average loss on ignition of about 8 per cent, which means that the ore is largely limonite

BRIQUETTING AND NODULIZING

W R Cox, New York, N Y —These get-together meetings are, in my opinion, going to be of considerable benefit to the operators of furnaces and mines It seems to me both necessary and advisable to become familiar with and to discuss the troubles and problems that both have to contend with

The concentrating and briquetting of magnetic concentrates, with which I have had experience at the Moose Mountain property in Canada, differs in almost every particular from the beneficiating methods Mr Harrison has just described The Moose Mountain crude ore, which averages about 33 5 per cent iron and 0 08 per cent phosphorus, is first crushed to −1-in ring and then ground in ball mills, 90 per cent passing a 200-mesh sieve Fine grinding is necessary if a high-grade concentrate averaging, say, 69 iron and 0 01 per cent phosphorus is desired In grinding to this fineness, the phosphorus content of the pulp is lowered by washing and the iron content raised by magnetic separation A large percentage of the concentrate will contain as little as 0 006 per cent phosphorus and as much as 71 per cent iron, and it has been demonstrated that the grade can be governed at will to average from 62 to 69 per cent iron and 0 02 to 0 01 per cent phosphorus, depending upon the fineness of the grinding The briquettes are 99 5 per cent hematite

There was some objection to the briquettes, one furnace operator thought that they were not a desirable blast-furnace material on account of their large size, and that a higher percentage of flue dust resulted when the briquettes were on the burden However, large-scale furnace tests indicated that the product was far from unsatisfactory when compared to the results obtained with the natural ores

As I remember, there was a material reduction in the coke consumption during the period in which the briquettes were being tested, say from an average of 2000 to as low as 1750 lb , and for certain periods as low as 1650 lb per ton of pig iron

I have made a few pillow-shaped briquettes about 2 in in cross-section in a roll press, and believe a method can be perfected to do this on a commercial scale   A briquette of this size and shape undoubtedly would be a more satisfactory burdening material, and should be produced at a lower cost, as the operation would be performed with much less labor   The principal cost of producing the large briquettes was due to the necessity for the hand piling and careful spacing of the 700 to 800 briquettes placed on each kiln car

Recently my attention was called to the practice at the Rouina iron mines (Africa), by Mr Joseph, and I found, in an article describing the briquetting method employed, the statement that a single laborer can easily handle the output of one press   The Moose Mountain records show that it required two and one-third men to perform this work   The Rouina kilns are 70 m. long, compared to 250 ft for those formerly operated at Moose Mountain, the capacity of Rouina is given as 220 tons for two kilns   The capacity of each kiln at Moose Mountain, charging at the rate of three cars per hour, was from 175 to 200 long tons per day.   Under 1920 operating conditions, the Moose Mountain cost for briquetting was estimated at $1 37 per long ton

In my opinion, the pressed briquette, when properly roasted, is superior to sinter, nodules or any of the natural ores, for the burdening of a blast furnace   In a thesis by Ludwig Mathesius written in 1913, mention is made of a number of experiments, relative to the reducibility of iron ores, sinter products and ore briquettes, in a current of gas, which demonstrated that pressed briquettes are the easiest to reduce through gas   The porosity of the briquettes is apparent from the fact that they readily absorb 30 per cent by volume of water and when exposed to the sun's rays lose all the contained moisture rapidly

Mr Williams' statement that briquetting methods have failed may be true for certain classes of products, but it does not apply to the method of briquetting magnetic concentrate that results in the production of a superior physical product, which I estimate can be produced at a cost of about one dollar per ton under present conditions   The pillow-shaped 2 by 2-in briquettes should be produced at a lower cost   Average sintering costs appear to be from 75¢ to $1 per ton

P. G HARRISON —I am curious to know how strong these briquettes are.   Can you throw them in a boat and pick them up again and will they hang together?

W R Cox —Yes   The briquettes that were tested by the Steel Company of Canada had been exposed to the weather for several years and only those that were not roasted at the proper temperature showed any signs of disintegration   I have briquettes in my office that were taken from the stock pile after 10 years of freezing and thawing weather, which show no signs of breaking up   It is, of course, essential that they should be roasted at the proper temperature

MEMBER —What is the temperature of firing the briquettes?

W R Cox —About 2100° F.

P. G HARRISON —Can you tell us why both briquetting and nodulizing have been tried for so many years, and, so far as I know, are practically an extinct practice so far as iron ore is concerned?   I am not criticizing, I want to know; it is worth money to me.

W R Cox —I am not holding any brief for briquettes, and believe that when the Moose Mountain property is again in operation sinter will be produced, notwithstand-

ing many reasons for believing that the physical qualities, especially porosity and reducibility, of the briquettes make them a superior blast-furnace product

P G HARRISON —If they will absorb water, I imagine there are   Does that answer also about nodulizing?

W R Cox —I made a study of the nodulizing process at Mayville and it appears that the product is at times raised to a melting heat, forming an iron silicate that is difficult to reduce in currents of gas   I believe furnace operators are of the opinion that nodules are not as easily reduced as other beneficiated products, they have a hard smooth surface

P. G HARRISON —In nodulizing, I believe that the mechanical process was never really worked out   I understand that rings always formed in the nodulizing kilns.

W R. Cox —There were all kinds of difficulties, both in Canada and in Mayville.

MEMBER.—Have you noticed any difference in the briquetting quality of, say, 60 per cent concentrate and a concentrate running 65 to 66?

W R Cox —Not in briquetting, but in sintering there would be a difference   I assume that you refer to the adhesive qualities in the presses   American Clay Manufacturing Co heavy-duty presses were operated and the briquettes were made under heavy compression   This is necessary because the briquettes must be fairly hard to withstand the piling by hand, they contained approximately 8 per cent moisture.   When a 60 per cent concentrate was produced at Moose Mountain, it was not necessary to grind so fine, but a good quality of briquette resulted   I have been grinding ores for forty-odd years and am not concerned over the costs of doing this work—they can be kept very low

P G HARRISON —Mr Cox, why did you load the cars by hand?   Why did you not load them by traveling belts?

W. R Cox.—They had to be piled and carefully spaced on the kiln cars, which are about 7 ft square, four or five tiers high, in order to allow the hot gases to pass freely to all briquettes   It was necessary to pile them carefully in order to obtain the best results   The pillow-shaped 2 by 2-in briquette, could, I believe, be made and dropped on a belt directly from the presses and be passed through a kiln or oven in a layer 5 to 6 in deep

P. G HARRISON.—You mean after you pressed them and before you heated them?

W. R. Cox —Yes   You understand that the cars enter the kiln at the cold end, near which a stack discharges the waste gases at a temperature of approximately 250°F.   Kilns of the well-known Grondahl type were used, fired with producer gas; the low temperature first dries and then heats the product to a cherry red just before the combustion chamber is reached   The cars are pushed forward at, say, 20-min intervals, three per hour, and when charged at this rate there were no soft or under-roasted briquettes, provided a uniform temperature of approximately 2000°F was maintained in the combustion chamber.   Underroasted, soft briquettes resulted when the charging period was lowered to 15-min intervals

P G HARRISON.—The briquettes are so soft before they are heated that they have to be piled by hand?

W. R. Cox.—The pressed, green bricks have to be handled very carefully; that was the reason for having so many men employed in this part of the operation   As a matter of fact, men cannot pile briquettes on 8-hr shifts without resting periods.

H J STEHLI, Montclair, N J —The nodules made in the rotary kilns show a very dense structure, and it is easy to understand how that would come about   Those nodules were formed by rolling in the kiln   They build themselves up just as a snow-ball does   They pick up material which is retained on the outside and condensed, making a sort of plastic coating   It is really a fusible slag that binds the ore particles together and makes a very dense structure that the gases cannot penetrate   That is probably the reason why the nodules never were a success

The briquettes to which Mr Cox referred are, I presume, what are known as the Grondahl briquettes, or something similar to them

W R COX —They were pressure briquettes—not Grondahl   The Grondahl presses operate with a hammer blow, and I believe that in his article Mr Mathesius makes a distinction between the two types

H J STEHLI —They were burned afterwards?

W. R COX —Yes

H J STEHLI —The structure of Grondahl briquettes shows a decided porosity, that is, the photomicrographs of the structure do

Mr Harrison asked about the function of water in the sintering charge   That is a difficult question to answer, but I think it can be put this way The function of water is to loosen up the charge; that is, to make it occupy more space   You can easily see the effect of this if you will fill a graduate with 100 c c of dry ore, take it out and moisten it with 10 per cent of water, then try to put it back in the graduate You may have as much as 150 c c   That is really the function of the water   It loosens the charge; makes air passages, which enable the ignition to take hold   If the charge is dry, there are passages for circulation of air and the ignition cannot be pulled down into the bed to set on fire

ORE DRESSING

C B. MURRAY —Mr Counselman, will you tell us something about ore dressing?

T B COUNSELMAN, Chicago, Ill —The matter of ore dressing as applied to iron ore is a distinct and peculiar thing   Those who have worked out West in the copper and lead and zinc country always are rather horrified by the metallurgy in the iron country   Yet there are very good reasons for current practice   First, there is the economic reason   You cannot afford to do things to iron ore, which is worth about two dollars a ton at the plant when you have finished with it, that you can afford to do with copper, for instance, which at present is worth about nine or ten cents a pound

The second point, of course, is that we have to deal with certain peculiar condi-tions   Nature did not make it quite as easy as she might have, or at least we have gone a long way toward exhausting all the ores that we could treat rather easily. We used to be able to wash out —100-mesh silica and call it a day   Most of that grade of ore is gone   We are beginning to realize now that it would be well to treat some of the ore that is hard to treat, before it is all gone   In other words, if we use up all the material from which we can make a good grade of concentrate with a low silica, and finally wind up with a lot of difficult wash ore from which we cannot make a concentrate that will come anywhere near the guarantees, we will be in a difficult position. Therefore all of the companies now, I believe, without exception, have built up more or less elaborate research staffs and are working on the more difficult ores. Some of these are jig ores, some are ores that require tabling. All kinds of methods are being tried, and some of the methods are rather complicated   Others

are very simple   I think we are going to find that we will have to do just as simple an operation as possible on iron ore if we are going to make a profit   Very often it pays to throw away as a tailing product, under present conditions, material that still contains quite a lot of iron   That was extremely well exemplified at Babbitt   There we crushed the ore to a relatively coarse size and made a rejection from 6 mesh up, of material that would average about 11 per cent magnetic iron   We had only 26 per cent magnetic iron to start with, so that on the face of it, it looked like poor business   Incidentally, we had trouble in convincing the fee owners that this method gave the maximum profit

The answer is simply this. If somebody made you a present of this material that contains 11 per cent magnetic iron, at the size at which we discarded it, you could not by any known method crush and concentrate that material to get out the iron and make any money   You would go very badly in the hole   Therefore, in all of the work on iron ore concentration, we have to use that same principle   We have to take out what we can get cheaply, and let future generations worry about the rest

In line with keeping our processes as cheap and simple as possible, I told Mr Coghill before this meeting that I was going to start a little discussion with him.   The thought I have in mind is this. Mr Coghill has advocated very close classification prior to tabling, on such ores as require tabling.   A good many years ago, before the advent of flotation in copper, we used to classify closely all our sulfide ores, elaborately treat them with various tabling processes, take out the primary slimes and concentrate these on vanners or slime tables   We did not have very good slime-concentrating equipment in those days, and we got about 65 per cent over-all recovery   Very shortly before flotation came in, I was connected with an operation in the Southwest where we inaugurated a roughing flow sheet   We crushed the ore to 4 mesh, put everything over the tables, slimes and all, and then ground the tailing to roughly 48 mesh   We then retabled the entire product of this regrinding, sands and slimes together   After we had done that, we had gotten out all of the coarse copper that was recoverable and there still remained some copper in the slime   So we made a sand-slime separation and did the best we could with the slime, which was not very much

We found, somewhat to our surprise, that we recovered much more −200-mesh copper on these two roughing-table operations than we could recover if we took out the slime at the beginning and treated it separately on machines designed for slime treatment   In other words, we trapped this −200 product and recovered it   As a result, we raised our over-all recovery from 65 per cent up to 83 per cent, which is pretty good work without flotation

I do not wish to be absolutely committed to this as my personal viewpoint, because there are a good many things to be said on both sides of the subject   However, I would like to ask Mr Coghill why it would not be a good idea to follow a somewhat similar procedure in his tabling work   In other words, instead of classifying the original feed into a large number of individual sizes, and treating each of these separately on tables that are adjusted to treat that particular size, why might it not be better to table the entire feed as a roughing operation, cut a middling and regrind it, if necessary, and then go to close classification?   In other words, stick to a simple flow sheet rather than a close-sizing flow sheet

SINTERING AT BLAST FURNACES AND AT MINES

Before yielding the floor, I want to express one more thought   Much has been said about the high cost of agglomerating on the Mesabi range   Sintering adds tremendously to the cost of iron ore as shipped down the lakes   It occurs to me that it might be highly desirable for the operators at the head of the lakes to ship the finer portion of their concentrated material to the furnaces for sintering   The coarse

portions, of course, are very desirable products, much like an old-range ore   The finer portion, I believe, without very much doubt can be sintered more cheaply at the furnaces than on the range, because coke breeze, which is essential for sintering, is available there at very low cost, and also usually an excess of blast-furnace gas which can be used for ignition   One mining company is doing that now   I have no idea what the economic results are   It seems to me that that is a point worth serious consideration

T L JOSEPH —What do you designate as fine material? Have you any size?

T B COUNSELMAN —What I meant by fine material is the product of the classifiers, about ¼ in and down   Log-washer or Dorr-washer concentrate, which, of course, contains a certain amount of material of that size and some finer, would be shipped direct   But everything recovered, beginning with the classifier rake product, plus the table concentrate, if any were produced, would then be shipped separately as a product to be sintered at the furnaces   Most of the furnaces have or are installing sintering plants to handle their flue dust
I am not sure of this, but I think it might be desirable to have some raw ore containing no carbon which would be mixed with the flue dust, serving two purposes, opening up the bed and lowering the over-all carbon content   I would like to hear from someone who has had experience on the sintering end

P. G HARRISON —I would like to know exactly what is back of the statement of cheaper cost of sintering at the furnace than at the mine   There are two costs of sintering, one the cost of producing sinter, which is cheaper in some plants than at the mine, the other, an offset   If you have an ore which loses 25 per cent of the bulk by sintering at the mine, you save in royalties and freight 25 per cent of $2 40, or whatever that differential is
Under such conditions I do not believe you could sinter more cheaply at the blast-furnace plant than you can at the mine   Some ore properties do not have a beneficiation clause in their leases, therefore they can make no saving in royalty   Some of us do   I know one person who did not have the beneficiation clause and could not get it, and therefore dismissed the possibility of sintering at his property.   Mr Counselman's idea of using the excess fuel in flue dust to sinter some of the fines of the ore coming down the lakes is obviously the cheapest method of sintering any ore material, because it is not necessary to buy any fuel

T. B COUNSELMAN —Your point is well taken, Mr Harrison   A washed ore has not the high moisture of a natural ore, and frequently does not have the combined moisture that many of the natural ores have   It is necessary to figure up for each property.   I think that on many properties it would be cheaper to sinter at the blast furnace
Of course, if the material is all ground to 100 or 150 mesh it cannot be shipped   The fine material that I spoke of sending down the lake to be sintered is the product from ¼ in down, which will not contain very much of the 150-mesh material   When first loaded into cars, it begins to drip   The water that runs out is reddish in color   In 20 min. to 2 hr , depending on the ore, the water that comes out is crystal clear   What happens is that the relatively coarser particles, around 10, 6 or 4 mesh, bridge over and form a filter bed, exactly like a sand filter for water, and hold the extreme fines   There is no puddling of that material in the cars   In fact, the cars can be heap-loaded, and will go down to the lake that way   By the time they get down to the lake, the ore has drained down to between 8 and 10 per cent moisture and is handled through the docks and out of the boats beautifully   This is actually being done   It was done all last season at one plant

MEMBER —I know that in Sweden that was tried years ago on very fine concentrates and two boats sank.

T. B COUNSELMAN —Yes, I know of the incident, too   When the Mesabi Iron Co started, that stuck out like a sore thumb, and we could ship the very fine concentrate in no other way than to agglomerate it.   The picture is entirely different in shipping this western Mesabi washed ore, containing material as coarse as ¼ or even ⅜ inch

SEGREGATION OF FINE MATERIAL

T L JOSEPH —I believe that the elimination or segregation of fine material is a step in the right direction, because if the fine material is mixed back into the coarser material, it increases the density of mass and it does not give as satisfactory a product physically as if the fine material were shipped down to the furnaces and sintered The tendency will be to produce more fine concentrates   Wherever possible, fine material should be handled separately and not mixed back in to bring the grade up on more siliceous material

T B COUNSELMAN —I agree with Mr Joseph   Something must be done about the recovery of the fine ore that is being lost on the range   The blast-furnace operators and the ore producers are all in the same boat and the more quickly we can find the solution, the better   Mr Williams remarked that if we can save all the fine iron that is being lost in the washing plants today, it would be equivalent to discovering 1,000,000 tons additional reserve of good wash ore every season   That cannot be done   But we can do the equivalent thing, if we save the fine iron   If we find some means by which we can get it into the blast furnace, with cooperation between the blast-furnace operators and the ore producers, we may accomplish something   As it is now, the steel manufacturers do not want the fine iron and iron-ore producers want to try to save it

RESEARCH NEEDED ON BLAST-FURNACE PRACTICE

R. H SWEETSER, Columbus, Ohio —We have heard a good many interesting things about beneficiation of iron ores and now we want to get some of this material into the blast furnace   At the Chicago meeting last September, and again last Friday in Pittsburgh, we heard a good deal about the effect of nodules and briquettes and sinter in the blast furnace   This afternoon we have had the idea expressed of opening up the burden in the blast furnace, and the question arises, will this prepared ore, the nodules and the briquettes and the sinter, in the opening up of the blast-furnace charge, help to produce more flue dust?   That is the question that is being studied now by some of the blast-furnace operators, and in some cases we find it does increase the flue dust a little   But there has not been enough change made in the furnace practice to adjust the practice to this condition of a more open furnace.   That is one of the troubles in our blast-furnace practice   We go by a sort of ratchet and pawl system   We improve somewhere and then we find we get another kind of trouble   We get an open structure and we find another set of difficulties   I think we will find the same thing in our blast-furnace construction   Brassert spoke of it recently [1]   He said that the progress of blast-furnace construction, the changes in lines, especially in the increase in diameter of the hearth, had brought about an ill-proportioned blast furnace, shaped like a bottle   He was discussing especially the

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[1] A. H. Brassert: Economical Aspects of the 1000-ton Blast Furnace   *Blast Furnace and Steel Plant* (1931) **19**, 89

thousand-ton blast furnace that was designed by the Chicago Committee of the Blast Furnace Association of Chicago   Dovel brings out the same idea when he says that they have increased the hearth diameter and the bosh diameter without increasing the top diameter   All of these things have to be adjusted   When we first used Mesabi ores, back in the nineties, the blast-furnace men had to learn how to use Mesabi ores   Many troubles came with the introduction of Mesabi ore and the blast-furnace practice had to be adjusted to it   Now we are getting beneficiated iron ores, which probably have been washed   The clay has been washed out and perhaps some of the silica   Then we get a very well prepared material   We have gone to the sizing of coke and we have taken out the breeze   In blast-furnace flux, in lime-stone, we have not progressed very far, because we do not know exactly what to do So that when we get a new product into our blast furnaces, it is up to the blast-furnace man to adjust his whole practice to take care of that product   Just because we do not have enough of the fundamentals of ferrous metallurgy, we are going at a good many of these problems blindly   It is hoped that in some of the work that is being carried on now by a special committee appointed by the President of the Institute there will be the study of a good many of the fundamentals of blast-furnace practice. We do not know enough of what goes on inside the blast furnace and it is in meetings like this, where the ore men get together with the fuel men and the blast-furnace men, that we are going to work out a great many of these problems

It is going to be more necessary than ever for the blast-furnace men to have more of this concentrated research work to test out the improvements in the preparation of beneficiated coking coals   We have the same problem there   Then we have to take up the problems of the beneficiation of the fluxing stone, and we have to work them all in together so that the blast furnaces of the future will not stop at 1000 tons a day We might as well, in this country, get ready for these bigger productions   The Germans are getting pretty heavy tonnage   I saw the other day a record of blast furnaces in India, making over 1100 tons of pig iron per 24 hours.

In this country we have to get our blast-furnace practice in line, and that means that we must do more research like that which has been done already by the Bureau of Mines

T. L. JOSEPH —In line with what Mr Sweetser has just said, I believe that there must of necessity be some improvement in blast-furnace practice by more attention to the physical characteristics of the materials, in order to make pig iron at the same cost that it is being made today, because it certainly is going to cost something to treat the leaner ores, and unless advantage is taken of certain changes in the physical character of the material as a result of concentration, the blast-furnace costs are going to increase, because the cost of the ore probably will increase   The Bureau of Mines has spent several years in laboratory work and in the field in trying to determine the conditions inside a blast furnace

Mr Sweetser pointed out that the furnaces today are operated to handle the particular kind of materials available. I believe that blast furnaces as a whole, operating on fine ores, must have some place in the furnace, a porous section, to act as a relief valve in order to force the large volume of gases to ascend through the charge without building up pressures. If we change the physical character of the material, it is possible that some section of the furnace which is porous is slightly plugged, so that the advantage of what appears to be a slightly coarser material such as sinter is lost   In other words, the usual blast furnace as charged has an enormous amount of segregation of fine and coarse material, and the big advantage, I believe, is going to come from paying more attention to the physical character of the material charged The sizing of material is very important for a number of reasons   It eliminates the segregation of fine and coarse material at the stock line and enables a better contact

between gas and solid and a more thorough preparation of the material in the top of the furnace. However, the sizing of fine lake ores is impracticable at the present time They cannot be sized because they contain too much fine material However, if in the course of beneficiation one-half of the material can be brought up to a size of $\frac{1}{2}$ in or more by agglomeration of fines, it will be feasible to charge the furnaces on sized ore and sinter I realize this is an ideal condition, but I believe that there is a definite trend in the industry towards coarsening up the material so that it may prove practicable to charge the coarse ore in separate sizes, along with sinter produced from fine ore and flue dust

Sizes of Limestone for Blast-furnace Use

Member —A nonferrous metallurgist asked me the other day if the very fine crushed limestone was taken out before the furnace was charged in ferrous metallurgy He said that it made a great difference in the production costs of lead and copper furnaces in the Southwest, when the very fine limestone was taken out and used in other places

R. H Sweetser —Generally the limestone is screened, taking out as much of the limestone dust as possible I do not know exactly the sizes, but most blast-furnace men want everything screened out below $1\frac{1}{2}$ in I think Mr Paul Hodges might say something about the sizes

P C. Hodges, Columbus, Ohio —We have been producing blast-furnace stone for a great many years, and this year we are putting into operation a new plant built especially with the idea of producing a more refined product for blast-furnace use

Some blast-furnace operators demand stone that is screened through a 5-in and over a $1\frac{1}{2}$-in screen, others want a smaller stone, through a 4-in and over a $1\frac{1}{2}$-in screen In our new plant, we are prepared to wash all sizes from 4 in down The minimum size now going into flux is that passing over a $1\frac{1}{2}$-in screen

Developing Ore Dressing of Iron Ores

W H Coghill, Rolla, Mo —I think the industry owes Messrs Mahon and Counselman a great debt for the paper they wrote on beneficiation of the iron ores [2]

As for the question Mr Counselman asked me, I can answer that entirely to my own satisfaction. But to go back a little bit, this relates strictly to ore dressing Ore dressing is just a branch of beneficiation It consists of making a physical separation between the mineral and the gangue, whatever the gangue may be The most common gangue in iron ores is silica The question is how should we go about it to outline a campaign for its separation? There are two systems that might be followed. We might begin research to undertake to develop some brand new scheme By that procedure we have a long period of investigation to find the method, and difficulties in the field follow those in the laboratory The other method would be to follow known processes. We would begin with the known and press into the unknown

In the first scheme we would undertake to press the unknown back in one fell swoop; we would come out with a brand new process In the second scheme, we would make gradual steps I admire a man who will go into the laboratory and try to bring out some new process for the dressing of the iron ores, but for my part I will follow the other system If an operator finds that his ore gangue can be removed

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[2] S. A. Mahon and T B Counselman· Washing Mesabi Iron Ores Abs, *Eng & Min. Jnl.* (1930) **130**, 519

by physical separation, I would advise him to put in a few jigs and get started   He will have enough trouble with that old process and whereas operators in other districts, districts other than iron ore districts, have followed ore dressing for years and years, and are still making improvements, the iron ore operators will find much to copy

The iron ore operators have not given attention to ore dressing   They have specialized in other lines and have become very proficient   But ore dressing is new to them   So I should say, start with jigging, and when jigging is going well, press along with efforts to improve   Then follow down through the system to the finer material and start tabling and work persistently year after year to improve the tabling   Proficiency in such simple processes as jigging and tabling is achieved only through years of struggle

Mr Counselman mentioned the 11 per cent material that goes to waste and cannot be retreated   Maybe that cannot be retreated, but possibly it could have been made to yield a profit while it was in the plant

After all, several steps in a flow sheet do not cost so much more than a few steps if the plant is properly laid out. In that connection, I think of the old Joplin district, now called the Tri-State district   I went before the operators there several years ago and said, "Your flow sheet is the most complex in the land "   At that time I thought that maybe we could develop grinding so that we could afford to grind to flotation size and could have an all-flotation plant and nothing but flotation, but I have given that up   They cannot economically simplify those flow sheets

They have roughing jigs and cleaning jigs, and sand jigs and chat jigs   They have tables, and then they have flotation   But what in the end? They are treating their ore only at the rate of 25 to 50 tons an hour, and the running cost is only 35¢ a ton   Yes, that 35¢ a ton would break some of the operators in iron ore work, but it would not be as much as 35¢ a ton for the iron ore operation   The fact is that the iron ore operators are loading free silica into their cars. The free silica may be removed cheaply

Whereas Mr Counselman's paper is splendid, I took his figures as a rebuke to the operators that they are satisfied to ship so much silica down the lake and pay the price   In order to market these high-silica products, they have to mix them in with low-silica ores   Furthermore, in regard to this thoroughness that I am advocating in milling, we so often stop without trying   A prominent operator once gave me one of the best lessons I ever had. He was suggesting that he would remodel a certain part of his flow sheet   I intimated what I had heard said so often   I said, "Yes, maybe you would get more mineral by doing it, but I expect it would cost you all that it is worth "   He replied, "We want to get the mineral and we will figure the cost afterwards "

Tabling and Classification

As for Mr Counselman's question relating to tabling, I can answer it so that you will get the point relating to tabling and classification   Hydraulic classification consists of sorting the mill feed so that the fine mineral is with the coarse gangue   This is easy to do because the heavy mineral falls faster in water than the light mineral   There results a series of products so sorted that the fine mineral is with the coarse gangue   The tables are eminently fitted for handling these sorted products because the table is a sizing machine   All the table has to do is to sort out that fine material and the job is done.

I will say just one more word about classification   I am afraid I did not finish what I intended to say. Whereas lead ores and the ores mentioned by Mr. Counselman are in themselves, generally speaking, classified products, your iron ores are of

the other order   Your best mineral and most of your mineral is in the coarse sizes
Of all things, the iron ores need classification because the fines are lean   When they
are fed to the tables unclassified the sizing action tends to size out the fine mineral,
to be sure, but the fine gangue comes with it, and the very best mineral is lost over the
sides of the table

I am fully aware that the iron country tried tabling some years ago and that the
tables were thrown out   Last summer I had the unfortunate experience of being
obliged to contend with those old tables after they were reinstalled   I do not wonder
that they were thrown out   Those tables were defective from the beginning   They
were built so that they could not be tipped enough to develop a side wash   The com-
pany with which we were cooperating bought some of those old tables   They had to
be revamped before they could be used   After all that fussing around, the company
shipped some of the Mesabi iron fines to their little 10-table plant and confirmed our
laboratory observations   They proved that they could remove much of the silica
and get a good grade of concentrate   The running cost within a large table plant
would not exceed 4¢ per ton of raw ore   The only alternative is to continue to waste
good fines in the sludge ponds

R H SWEETSER —If an ore had clay in it, could a jig be used?

W H COGHILL —Log washing would precede the sort of milling I was talking
about   Log washing would come first to remove the clay

DIRECT REDUCTION AND CONCENTRATION

W H SMITH, Detroit, Mich —Mr Williams' paper does not give consideration
to the progress made in the bene᪉ciation of iron ores by reduction, and the merits of
that product for blast-furnace use, that is, to the work done by the General Reduction
Corpn as published in January [3]   That article gave the results and treatments of
many ores from different parts of the world where the iron oxides have been reduced,
and a percentage of the gangue removed prior to the charging into the blast furnace
for slagging and melting   By this method there is less sulfur than when reduction
and melting is carried on in a single operation, as less than one-half the amount of coal
is required and that so prepared that a greater percentage of the sulfur as originally
present does not come in contact with the reduced iron   Also, by this method, the
iron after reduction is prepared into suitable sizes, so that when charged into the blast
furnace or cupola the blast or heat flow is in the highest ratio of efficiency.   Iron so
prepared and used as a blast-furnace charge has no oxygen and fewer impurities to
encounter in slagging and melting, consequently the product is better, and will
ultimately obtain an economic place in the regaining of iron.

COST A CONSIDERATION

C E WILLIAMS (written discussion) —With reference to Mr. Cox's statement
regarding briquetting, I said that previous attempts to produce briquettes at rea-
sonable costs have failed   I know of no briquetting process now in commercial
use or of one that produces a product better suited for blast-furnace use or cheaper
than sinter

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[3] G. B Waterhouse. Iron Ores Beneficiated by Direct Reduction and Concentra-
tion   *Iron Age* (1931) **127**, 161.

My statement concerning the application of sponge-iron processes to the beneficiation of iron ores was made after giving consideration to the process referred to by Mr. Smith   It is difficult to follow Mr Smith's reasoning that less sulfur is introduced when the reduction and melting are carried out separately   No substantiating data are given in the report he mentions   Treatment of lean ores at the high temperature and in the highly reducing atmosphere required for reduction of iron oxide to metal would appear to be an expensive method of preparation, prior to concentration, of a product so cheap as iron ore

A Statistical Analysis of Blast-furnace Data

By RICHARD S MCCAFFERY[*] AND RONALD G STEPHENSON,[†] MADISON, WIS

THE statistical analysis of blast-furnace data was undertaken to determine some of the relations which exist between the variables involved in furnace operation, and particularly to show the effect of variation of slag composition on such economically important factors as coke consumption, daily tonnage of pig iron and sulfur elimination It was desired to correlate the results obtained in commercial practice with those predicted from a study of the quaternary system lime-alumina-silica-magnesia

This paper presents the results of a preliminary study of blast-furnace daily operating reports, and is intended to indicate the suitability of our method of attack and something of the results that may be expected from an extended statistical examination of such data

It has been shown that blast-furnace slags are not composed of oxides, as reported by chemical analysis, but are actually composed of several compounds, each made up of two or more of the oxides present [1] These compounds persist in the liquid state, and the properties of a slag are the properties of a mixture of these compounds, and not of a mixture of the ultimate oxides [2,3] The oxides lime, alumina, silica and magnesia make up 94 to 96 per cent. of the usual blast-furnace slag, and assuming that we may neglect the remainder of the components, we may determine the minerals present, and their relative proportions, from a study of the quaternary system involving these four oxides.

Operating reports from 15 furnaces were available for this investigation. Complete slag analyses for one slag per day were available, permitting the calculation of the mineral composition of the slags used. Basic, malleable and foundry irons, with silicon varying from 0 75 to 4.50 per cent were included in the reports for this examination.

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[1] G A Rankin and F E Wright The Ternary System, CaO-Al₂O₃-SiO₂. *Amer Jnl Sci* (1915) **39**, 58

[2] A L Feild and P H. Royster Slag Viscosity Tables for Blast-furnace Work U. S. Bur Mines *Tech Paper* 187 (1918) 7

[3] R S McCaffery, J F Oesterle and L Schapiro Composition of Iron Blast-furnace Slags A I M E. *Tech Pub* 19 (1926)

METHOD OF CLASSIFICATION

Due to the quantity of data and the number of variables to be compared, the method of electric tabulating and accounting machines of the International Business Machines Corporation was adopted   This method involves the use of three machines—a key punch for recording the original data on tabulating cards through the medium of punched holes, a sorting machine which arranges and classifies the cards, and a printing machine which makes a record of the data from the sorted cards   Work was begun on the 45-column tabulator, which was provided for part-time use by the Accounting Department of the University

The cards were punched with the code number of the plant and of the individual furnace, the date and other operating data   Moisture content of the air was expressed in grains per cubic foot   Only whole numbers were used, the figures reported being corrected to the nearest unit.   The value punched on the card is the average between the day and the night moisture determination

Fractional tonnage has been corrected to the nearest ton   Coke per ton of pig (the units figure has been omitted) is the average number of pounds of coke consumed per long ton of iron produced

The settling rate is the number of charges per 24 hours

Silicon, sulfur and manganese in the pig were recorded to two decimal places, and phosphorus was recorded to three decimal places.

The slag sample analyzed for the report is taken once during the day.   In order that all analyses compared might be related as closely as possible, the metal analysis for the cast and the slag sample taken at the time of the cast were punched on the cards, rather than an average metal analysis for the day.

Slag content of iron, expressed as FeO, manganese as Mn, and sulfur as S, have two decimal places each.

For the slag composition ranges which have so far been examined, the original tetrahedron designating numbers[4] have been retained

Mineral composition, rather than oxide composition, has been recorded on the cards   Decimal percentages of minerals are omitted.

There are a great number of factors acting simultaneously to influence the operation of a blast furnace, and in order to make a comparison between two variables and find how the variation in one affects the other, it was necessary to eliminate the effects of variables which were not being considered.   This was done by selecting for examination those reports in which the variables it was desired to eliminate were approximately constant in value.   The selection of the suitable reports from the mass of data was done with the mechanical sorting machine

In principle the method of classification may be represented as follows:

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[4] R. S. McCaffery, J. F. Oesterle and L Schapiro *Op cit.*

Let A, B, C, D be variables   We wish to find the relation of A to B, A to C, A to D, etc   To compare A and D, independent of variations in B and in C, we hold these last two variables at constant values while we vary A and D We first divide the data into groups with respect to C, in any one of which the values of C will be within chosen limits   We then subdivide these groups with respect to the variable B into a suitable number of classifications, in which the variable B is constant within chosen limits   If we make 10 divisions with respect to C, and 5 with respect to B, there will result 50 groups of data, in any one of which both B and C are approximately constant, and we can examine each of these groups separately for the relation between variables A and D.

Curves can be plotted using values of A and D as axes, and the curves will show the relation of A to D independent of the effect of variations in B or C. By plotting several of the curves for differing values of B or C on the same sheet, the effect of variation in one of these variables will be indicated by the displacement of the curves

The number of variables that can be compared and examined by this method depends only upon the amount of data available.

To calculate the mineral composition of a slag, it is convenient to follow the procedure outlined below·

1. Recalculate the composition of the slag, neglecting the constituents other than the four oxides—lime, alumina, silica and magnesia   The sum of the percentages of the recalculated oxides should equal 100 per cent

2. Locate the position of the recalculated analysis in the slag model,[5] which is the constitutional diagram for the four-component system lime-alumina-silica-magnesia   .

3. Determine by inspection what minerals form the corners of the inner tetrahedron within which the given slag is located.

4. The formulas for this tetrahedron are used to calculate the mineral composition of the slag   If the proper tetrahedron is not selected, the mineral composition cannot be correctly calculated, some of the values will be negative and the sum of the percentages of the minerals will not be 100 per cent   ·

COMPUTATION OF MINERALS PRESENT

Having recalculated the oxides on a 100 per cent. basis and determined the proper set of formulas, the percentages of the minerals present may be computed readily   The formulas given in Table 1 are in their simplest form, and were obtained by reduction of the formulas for the calculation of mineral composition given in A. I M E. *Technical Publication* No. 19.

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[5] R S McCaffery, J. F Oesterle and L. Schapiro. *Op cit.*

TABLE 1 —*Mineral Composition Formulas*

TETRAHEDRON 6

Akermanite	6 7613 MgO
Calcium bisilicate	5 8018 − 11 5629 MgO − 9 9455 CaO − 4 6601 Al₂O₃
Gehlenite	2 6896 Al₂O₃
Tricalcium disilicate	4 7977 MgO + 9 9429 CaO + 1 969 Al₂O₃ − 4 8005

TETRAHEDRON 8

Akermanite	6 7613 MgO
Calcium orthosilicate	17 1449 MgO + 14 7468 CaO + 6 9098 Al₂O₃ − 8 6026
Gehlenite	2 6898 Al₂O₃
Tricalcium disilicate	9 6051 − 23 9098 MgO − 14 7502 CaO − 9 6009 Al₂O₃

TETRAHEDRON 2

Akermanite	6 7613 MgO
Anorthite	2 3143 − 0 9493 Al₂O₃ − 4 7934 CaO − 2 3133 MgO
Calcium bisilicate	0 9666 + 0 0692 CaO − 2 6765 Al₂O₃ − 6 7302 MgO
Gehlenite	2 2789 MgO + 4 7238 CaO + 3 6251 Al₂O₃ − 2 2805

TETRAHEDRON 5

Akermanite	2 2683 + 0 1623 CaO − 6 2803 Al₂O₃ − 9 0283 MgO
Anorthite	2 3142 − 0 9488 Al₂O₃ − 4 7939 CaO − 2 3129 MgO
Gehlenite	3 6269 Al₂O₃ + 4 7249 CaO + 2 2806 MgO − 2 2815
Monticellite	9 0614 MgO + 3 6034 Al₂O₃ − 0 0932 CaO − 1 3014

TETRAHEDRON 13

Anorthite	4 6322 − 7 3672 Al₂O₃ − 4 6267 CaO − 11 5396 MgO
Gehlenite	3 6302 Al₂O₃ + 4 7239 CaO + 2 2864 MgO − 2 2825
Madisonite	10 955 Al₂O₃ − 0 2834 CaO + 15 7480 MgO − 3 9562
Monticellite	2 6070 − 7 2188 Al₂O₃ + 0 1868 CaO − 6 4957 MgO

TETRAHEDRON 7

Akermanite	9 0768 − 13 9391 CaO − 9 0729 Al₂O₃ − 15 8355 MgO
Calcium orthosilicate	5 9353 CaO + 1 1746 Al₂O₃ + 2 8637 MgO − 2 8651
Gehlenite	2 6898 Al₂O₃
Monticellite	8 0036 CaO + 5 2096 Al₂O₃ + 12 9737 MgO − 5 2118

The tetrahedrons for the determination of the mineral composition of iron blast-furnace slags are listed in order of importance, the slag compositions falling within tetrahedrons 6, 8 and 2 being common in American practice. The formulas are in a form suitable for rapid calculation, and, using a calculating machine, the time required to calculate the mineral composition of a slag is about three minutes.

Example

Assume a blast-furnace slag of the following composition: SiO₂, 37.40 per cent , Al₂O₃, 12 00; CaO, 43 00; MgO, 4 56, FeO, 0 91; MnO, 0 52, CaS, 1.58, total, 99.97 per cent

The lime, alumina, silica and magnesia are totaled, giving a sum of 96 96 per cent The remainder of the slag is neglected for the purpose of mineral calculation, and the percentages of the four significant oxides are each divided by 96 96, and multiplied by 100 to give the composition of the slag in terms of 100 per cent. of these four oxides It is sometimes more convenient to determine the reciprocal of the sum and then the

correction to the 100 per cent basis can be effected by multiplication rather than division

The recalculated oxide composition is: SiO_2, 38 57 per cent.; Al_2O_3, 12 38; CaO, 44 35; MgO, 4 70, total, 100 00 per cent

The position of a slag of this composition is located in the model,[6] and the tetrahedron number is determined by noting the minerals forming the corners of the inner tetrahedron in which the slag is included The above slag will be found to fall within the boundaries of tetrahedron 6. The formulas applying to this tetrahedron may then be applied to find the proportions of the various minerals present in the slag

The percentage of the mineral Akermanite in the slag is determined by multiplying the recalculated value of the magnesia by 6 7613

$$6\ 7613 \times 0\ 470 = 31.78 \text{ per cent. Akermanite}$$

The proportion of tricalcium disilicate is determined by substituting the recalculated oxide values in the fourth equation of tetrahedron 6:

$$4\ 7977 \times 0\ 0470 + 9\ 9429 \times 0.4435 + 1\ 969 \times 0\ 1238 - 4\ 8005 =$$
$$7\ 84 \text{ per cent. tricalcium disilicate.}$$

Similarly, for Gehlenite·

$$2.6896 \times 0\ 1238 = 33\ 30 \text{ per cent Gehlenite}$$

and for calcium bisilicate:

$$5\ 8018 - 11\ 5629 \times 0\ 0470 - 9\ 9455 \times 0\ 4435 - 4\ 6601 \times 0.1238 =$$
$$27\ 06 \text{ per cent calcium bisilicate}$$

This calculation is checked by totaling the calculated percentages of the four minerals. The sum should fall between 99 95 per cent and 100.05 per cent., as follows.

	PER CENT
Akermanite .	31 78
Tricalcium disilicate	7 84
Gehlenite .	33 30
Calcium bisilicate .. .	27 06
	99 98

In case the oxide composition of a slag is such that the point representing that composition in the model is on or near the boundary plane of two tetrahedrons, it is sometimes difficult to determine which set of formulas must be applied to calculate the mineral composition. There are three minerals common to two adjacent tetrahedrons. The fourth mineral of each is different, and by the application of one of the formulas which is not common to the two tetrahedrons the proper choice can be made. If the value, upon completion of the calculation, is found to be negative, the wrong tetrahedron has been chosen, and the correct mineral

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[6] R. S. McCaffery, J F Oesterle and L Schapiro *Op cit.*

calculation requires the application of the group of formulas belonging to the proper tetrahedron.

EFFECT OF SILICON

The curves which are presented indicate the importance of the grade of iron made in determining operating conditions, and no comparison of variables was possible without first grouping data with respect to silicon

Increase in silicon in the pig is accompanied by a slight decrease in daily tonnage of iron   This decrease amounts to about 2 per cent per day for each 1 per cent increase in silicon (Fig 1)

Silicon in Metal

Tonnage	.75	1 00	1.25	1 50	1.75	2 00	2 25	2 50	2 75	3 00	3 25	3.50	3 75	4 00	4.25	4.50
									1		2					
440									1		1					
				1			1	1				2				
460											1					
											1					
480					1	2			1							
								2	1	2			1	1		
500		2	1			3	5	4	1	2	3		1	1	1	
		2	1	1	1	7	3	1	2		3	1	1			
520		4		2	3	3	6	2		2	4	1				
		2	2	2	1	1	3	8	6	9	2	2	1	1		
540	1		1	2	2	4	3	5	10	6	4	5	4			
	1	1	2	1	6	5	13	13	7	9	6	1				
560	1	2		6	2	6	10	9	7	6	4	2				
	2	2	4		2	7	8	7	13	11	1	1				
580	6	2	3		5	7	11	9	9	4	3					
		3	3	3	5	8	15	11	4	5	1		1	1		
600	3	1	2	3	7	6	9	8	7	5	2	2				
	3	3	2		3	4	6	6	5	3						
620	1	3	3		2	2	5	7	4	2						
	2	1		2	3	2	3	2	1	2						
640		1					2	2			1					
	1				1			1			1					
660					1	1	3				1					
	1					1	2			1						
680			1			1	1	1								

Curve shows general trend.

Figures indicate number of cards in each classification

(Y-axis: Tonnage per day of Metal produced)

FIG 1—RELATION BETWEEN SILICON IN METAL AND DAILY TONNAGE OF IRON

The consumption of coke per ton of iron is increased 100 lb for each 1 per cent increase of silicon (Fig 2).   A German investigator[7] reports that every 0.30 per cent. increase in silicon causes an increase in coke consumption of 20 lb per ton of pig.

Sulfur elimination varies directly with silicon.   This is not so apparent from an examination of sulfur in the metal, but is indicated by a greater concentration of sulfur in the slag, as shown by Fig 3   Sulfur in the slag approaches a limit of 2 20 per cent. as silicon increases to the maximum of 4 25 per cent.   Sulfur in the metal does not change materially

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[7] G V Slottman. Gas Analysis Index to Furnace Operation   *Blast Furnace and Steel Plant* (1928) **16**, 615–616

Silicon in Metal

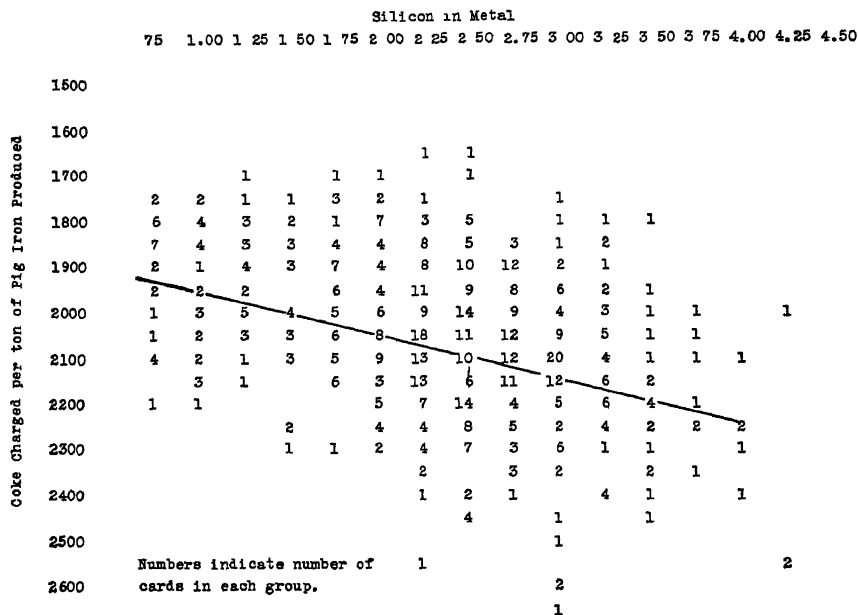| Coke Charged per ton of Pig Iron Produced	.75	1.00	1.25	1.50	1.75	2.00	2.25	2.50	2.75	3.00	3.25	3.50	3.75	4.00	4.25	4.50
1500																
1600																
						1	1									
1700			1		1	1		1								
	2	2	1	1	3	2	1			1						
1800	6	4	3	2	1	7	3	5		1	1	1				
	7	4	5	3	4	4	8	5	3	1	2					
1900	2	1	4	3	7	4	8	10	12	2	1					
	2	2	2		6	4	11	9	8	6	2	1				
2000	1	3	5	4	5	6	9	14	9	4	3	1	1		1	
	1	2	3	3	6	8	18	11	12	9	5	1	1			
2100	4	2	1	3	5	9	13	10	12	20	4	1	1	1		
	3	1			6	3	13	6	11	12	6	2				
2200	1	1				5	7	14	4	5	6		4	1		
				2		4	4	8	5	2	4	2		2		2
2300			1	1	2	4	7	3	6	1	1			1		1
						2		3	2		2	1				
2400					1	2	1			4	1			1		
							4			1		1				
2500										1						
Numbers indicate number of cards in each group.						1									2	
2600										1						
										2						
										1						

Fig 2 —RELATION BETWEEN SILICON IN METAL AND COKE CHARGED PER TON OF PIG PRODUCED

Silicon in Metal

Sulfur in Slag, Per Cent	.75	1.00	1.25	1.50	1.75	2.00	2.25	2.50	2.75	3.00	3.25	3.50	3.75	4.00	4.25	4.50
1.00											1					
1.10																
1.20							1	1	1							
1.30	2			1			1									
1.40	7	6	7	1	1	1		2	1							
1.50	3	9	3	2	4	5		3								
1.60	2	2	3	2	6	5	4	2	2	1	1					
1.70	2	3	1	6	6	8	5	4	5	2	1					
1.80		1	3	6	6	6	13	12	3	8	2	1				
1.90		1	5	1	9	9	14	12	13	9	5	1	1			
2.00		2	1	1	6	9	13	18	12	7	7	2				
2.10				2	3	3	18	14	11	11	6	4		1		
2.20						4	10	11	9	11	6	1	2			
2.30			1	1	1	3	11	11	7	5	4	3	1	1		
2.40						3	3	2	10	7	3	3	1			
2.50					2	2	5	7	2	6	1	1	1			
2.60							5	6	4	4		1				
2.70				1	1	4		1	2	2			1			
2.80					1	1	1									
2.90										1	1	2				
3.00																
3.10																

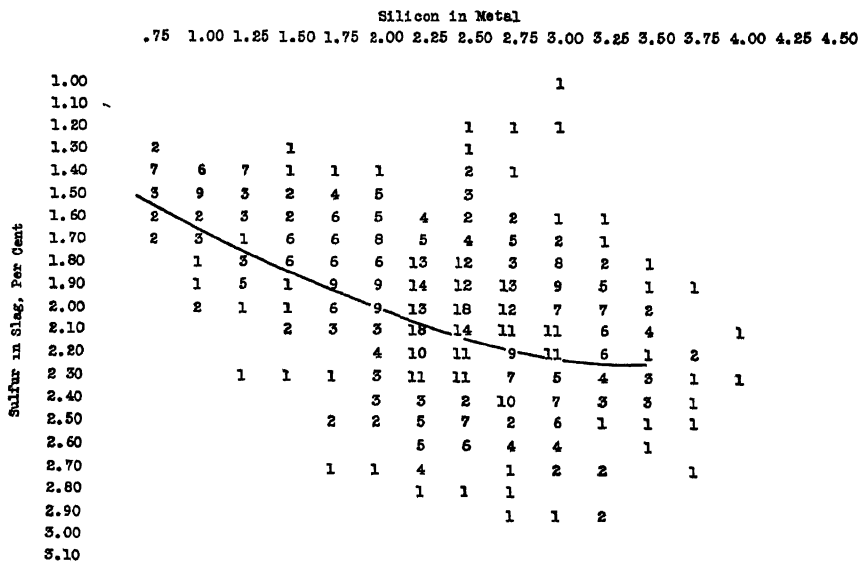Figures indicate number of cards in each group

Fig 3 —RELATION BETWEEN SILICON IN METAL AND PERCENTAGE OF SULFUR IN SLAG

The ratio of sulfur in the slag to sulfur in the metal also increases with silicon content of the metal. (See Fig 4.) Since the values given for sulfur represent concentrations of this element in slag and metal, the ratio is a measure of its distribution.

In each of the above comparisons, the results plot as wide bands and the curves are determined from weighted averages. The presence of bands instead of lines indicates the effect of other important variables, and Fig. 5 shows the results obtained by plotting the data with respect

Silicon in Metal

Ratio	.75	1.00	1.25	1.50	1.75	2.00	2.25	2.50	2.75	3.00	3.25	3.50	3.75	4.00	4.25
20				1						1					
				1			1								
30	2	3	3	1		1	1								
	7	5	1	3	1	1			2	2					
40	1	2	3	2	3	9	7	2	2						
	3	4	1	1	9	6	7	10	3	1	2				
50	3	4	5	3	8	9	11		6	4	2		1		
		3	4	3	9	6	14	14	5	5	2	1			
60		2	5	3	3	6	15	19	10	11	4	1	1		
		1	1	1	7	7	13	10	14	5	5	3	2		
70				2	2	5	11	18	10	8	5	2			
					2	4	10	12	7	11	6	3			
80					2	5	3	8	8	3	2			3	
			1	1		5	2	8	6	1	1				
90				1		1	3	5	2	3	2	1	1		
			1			1	4		1	4	2	1	1		1
100						1	1		2		1				
110									1	2	3			1	
									1	1	1				
120									1	1	1				1
						1			3	2			1		1
130									1						
140									1						

Curve Shows General Trend
Figures indicate number of cards in group.

FIG 4 —RELATION BETWEEN SILICON IN METAL AND SULFUR RATIO

to slag composition and silicon content of the metal. By plotting sulfur ratios on triaxial diagrams of mineral composition, with one of the minerals and the silicon content of the metal at constant values, it was found that the sulfur ratios were larger on the lime side of tetrahedron 6 than on the silica side (Fig. 6). Plotting these ratios of sulfur distribution against percentage of calcium bisilicate in the slag, it was found that increase in this mineral was accompanied by a decrease in sulfur ratio for any given grade of iron. In Fig 5 the slope of the curves is due to the change in slag composition, and the vertical displacement of the curves is due to the difference in hearth temperatures necessary to reduce various amounts of silicon into the metal.

S in Slag
S in Met.
50

175-200% Si

200-225% Si

60

225-250% Si
250-275% Si

275-300% Si

70

325-350% Si

80

90

Acidity ⟶

100

5   10   15   20   25   30   35   40
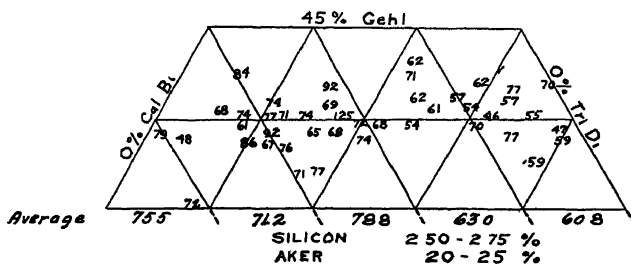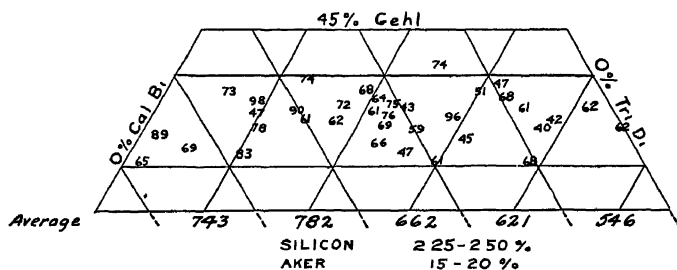
% of Calcium Bisilicate

FIG 5 — RELATION BETWEEN SILICON IN METAL AND SLAG COMPOSITION FOR SLAGS
IN TETRAHEDRON 6

45% Gehl

0% Cal Bi.   0% Tri Di.

73   74   68   51 47
98   72 64 75 43   68
47 90   61 76   61
89   78   62 69   96   42   62
65   69   83   66 59   45   40
47 61   68

Average   743   782   662   621   546

SILICON   225-250 %
AKER   15-20 %

45% Gehl

0% Cal Bi.   0% Tri Di.

84   62
71
68   92   62 62   70
74   69   57 77
73 48 61 62 77 71 74 125 68 54 57 46 55
86 61 76   65 68   74   70   77   47 59
71 77   59
72

Average   755   712   788   630   608

SILICON   250-275 %
AKER   20-25 %

FIG 6 — REPRESENTATIVE PLOTS, TETRAHEDRON 6
Numbers indicate ratio of sulfur in slag to sulfur in metal

The effect of calcium bisilicate on sulfur distribution may be due to any one or to a combination of these three causes:

1 Slags high in calcium bisilicate contain less lime than those low in this mineral   If lime and not calcium bisilicate were the determining factor, calcium bisilicate would still be an inverse measure of the amount of lime in the slag within the limits of tetrahedron 6.

2 If sulfur distribution between metal and slag reaches an equilibrium, the equilibrium concentrations may change with change in mineral composition   Schenck, Franz and Willeke[8] indicate that such shifts in the equilibrium concentrations in iron oxide-carbon monoxide equilibria may be caused by the presence of magnesia, silica, lime, alumina and other oxides

3. According to Clements[9] calcium bisilicate dissociates very little Increase in this mineral will therefore decrease the available lime in the slag, in addition to measuring a decrease in percentage of lime.

The effect of higher lime slags in increasing the sulfur distribution ratio is continuous across the boundaries of tetrahedrons 2 and 8   This relation is brought out in the following comparison.

COMPARISON OF SULFUR RATIOS IN TETRAHEDRONS 2 AND 8

The sulfur ratio is obtained by dividing the sulfur content of the slag by the sulfur content of the metal   The sulfur ratios given in Table 2 are averages for all data falling within the tetrahedrons 2 and 8.

TABLE 2 —*Comparison of Sulfur Ratios in Tetrahedrons 2 and 8*

Silicon in Metal, Per Cent	Ratio in Tetrahedron 2	Ratio in Tetrahedron 8
1 25–1 49		
1 50–1 74		
1 75–1 99	40	80
2 00–2 24	45	77
2 25–2 49	60	85
2 50–2 74	47	70
2 75–2 99	60	96
3 00–3 24	60	92
3 25–3 49	58	110

In all cases the average of the sulfur distribution ratios was higher when the furnace operated with slags occurring in tetrahedron 8 than when the more siliceous slags of tetrahedron 2 were employed.

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[8] Von R Schenck, H Franz and H Willeke Gleichgewichts-untersuchungen uber die Reduktions—Oxydations—und Kohlungsvorgange beim Eisen, ix *Ztsch anorg u allg Chem.* (1929) **184**, 1

[9] F Clements Blast Furnace Practice **1**, 124–125 London, 1929   Ernest Benn, Ltd

Slag composition varies over considerable ranges during the course of a day. Tonnage of iron produced and coke consumed are values which result from the integrating of all factors influencing furnace operation, and if the slag sample which is analyzed daily does not represent a mean from which the deviation is small, it is not likely that the effect of different slags on tonnage or coke consumption can be brought out   The slag data seem most useful when compared with factors measured at the same time the slag sample is taken.

The method of attack which has been proposed for the investigation of iron blast-furnace data will permit the examination of a large number of reports.   Additional reports will permit a more effective application of the methods of examination which have been outlined, and will bring out relations now obscured

DISCUSSION

(T L Joseph presiding)

R H SWEETSER, Columbus, Ohio —This is a splendid method of presenting and studying a lot of data   My objection to it is that it ignores the composition of the coke   This is important because the amount of coke used establishes the tonnage of pig iron produced

The increased cost given for each per cent of silicon may not be true   Changes in mixture may cause as much coke to be used in making low-silicon as high-silicon pig iron, though usually less coke is used for the low-silicon iron   The same is true for production rates   The method would be all right if applied to one furnace but not to fifteen.

W H SMITH, Detroit, Mich —Slag studies should be made in the laboratory

T L JOSEPH, Minneapolis, Minn —I am very much in favor of laboratory work to get data to correlate blast-furnace operations with fundamental information. Blast-furnace operators must produce pig iron containing specified amounts of silicon and sulfur   This is largely accomplished by proper regulation of the temperature and physical and chemical properties of the slag   If studied and applied, the information which Professor McCaffery and his coworkers have contributed on the viscosity of slag containing widely varying amounts of SiO_2, Al_2O_3, CaO and MgO should lead to a more definite correlation of slag properties and silicon and sulfur control

R. S McCAFFERY —In reply to Mr Sweetser, I should like to have more data and with sufficient averages could draw better conclusions   The paper was presented as an example of method of study

I N GOFF, Indiana Harbor, Ind (written discussion) —This paper correlates a vast amount of iron blast-furnace data in order to show the effect of slag composition upon furnace operation.   It is of unusual interest to us because we have been working along the same general line during the past few years.

Our data obtained from blast furnaces making standard basic pig iron have shown curves of the same general trend as those on Figs 1, 2, 3 and 4.

By plotting the ratio $\dfrac{S- \text{in slag}}{S- \text{in metal}}$ with respect to anorthite and using silicon contents in the metal within the range of standard basic iron, we obtain curves which

show a decrease in the sulfur ratio as the anorthite increases   At the same time the
slope of these curves increases as the silicon in the metal decreases   The following
points are brought out by our curves which agree in general with the curves of Fig 5

1 The ratio $\dfrac{\text{S- in slag}}{\text{S- in metal}}$ decreases as the anorthite content of the slag increases

2 High-anorthite slags are characterized by low lime and high silica

3 The viscosity of the slag increases with the anorthite content

4 With increasing viscosity we may expect irregular furnace operation and
decreasing tonnage

We have made a comparison of the ratio $\dfrac{\text{S- in slag}}{\text{S- in metal}}$ in tetrahedra Nos 2, 6 and 8
when the furnaces were making standard basic iron   Our data show that slags with
the highest sulfur distribution ratio were in tetrahedron 8, those in No 6 show a
decrease in this sulfur ratio, and slags in No 2 show the lowest ratio   This agrees
with the findings of McCaffery and Stephenson in Table 2, although they have not
included tetrahedron 6 in their comparison   Our work has been confined to standard
basic iron in which the silicon content is below the range investigated by these authors

A study of slags obtained from approximately 600 casts of basic iron, with the
magnesia content in the slag between 1 25 and 2 00 per cent, has brought out facts
leading to the following conclusions

1 The average largest tonnage of iron was made when the slag composition was
in No 6 tetrahedron. The tonnage decreased when the slag was in tetrahedron
No 2 and was still less for No 8

2 When furnaces were operating abnormally the slag composition was usually
found to be in tetrahedron 2   This emphasizes the importance of the slag viscosity
and the effect of anorthite

Air Discharge of Circular Tuyeres

By Richard S. McCaffery* and Daniel E. Krause,† Madison, Wis

There has been some discussion among blast-furnace operators regarding the relative merits of tuyeres of the converging type and tuyeres designed in an attempt to produce a diverging jet of air An article[1] on Progress in German Blast Furnace Practice indicates the interest in this subject abroad   This article illustrates a diverging type of tuyere which is shown here in Fig 1A   The design appears to be rather poor as regards known properties of air flow   The adoption of this tuyere, the article states, resulted in a decrease of blast pressure of about 4 lb per sq in and an increase of the output of the furnace   If the improvements mentioned are due entirely to the change in tuyere design, the subject of tuyere design seemed worthy of investigation and this paper is a report of such work.

Because of the gain in efficiency brought about by the use of a diverging tuyere in the German plant, it was thought desirable to investigate the shape of the air streams issuing from various types of tuyeres to ascertain whether the gain was due to the tuyere itself or to the distribution of the air in the furnace   Since it is difficult to do experimental work on a full-sized furnace, or even on full-sized tuyeres, and because of the equipment available for the work, it was decided to carry out the work on scale models of tuyeres   Therefore, in this work, single tuyeres were used and the blast discharged into the atmosphere   The shape of the air stream was determined by means of a Pitot tube suitably supported in the air stream at various positions   The air was furnished by a Roots blower driven by a 10-hp. direct-current motor having field control, and capable of discharging 250 cu ft. per min with a pressure on the discharge of 4 in. of mercury.   A modern blast furnace with 21-ft hearth requires about 50,000 cu. ft. per min of free air at from 16 to 23 lb per sq in pressure, depending upon the type of burden   This pressure is the total pressure required to force the air through the burden and through the tuyeres   Upon computation the pressure drop through the tuyeres is about 1 to 2 lb per sq. in.   By making the tuyeres to a one-fifth scale, and by using a pressure of 1.5 in of mercury, the shape of the air streams should be

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[1] H. A Wagner Progress in German Blast Furnace Practice. *Blast Furnace and Steel Plant* (1929) **17**, 81.

similar to those of larger tuyeres. The conditions, however, are not the same as in a blast furnace because of the medium into which the air is discharged

A 3 by 6-ft air receiver was mounted on the blower in order to reduce pulsations from the blower. Following the air receiver, the air passed through an orifice meter, which is described at the end of this paper From the orifice meter, the air passed through an elbow and 6 ft. of 6-in
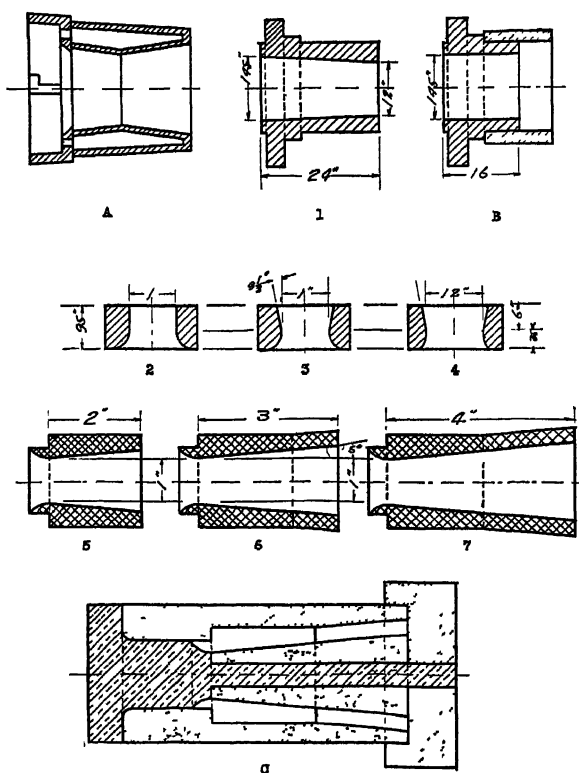
FIG 1—DETAILS OF SOME OF THE TUYERES USED

A Tuyere shown in *Blast Furnace and Steel Plant* (Jan , 1929)   No dimensions given
B Fixture for diverging tuyeres   No 3 Model proposed for some plants
No 1 Standard tuyere   No 4 Similar to No 3
No 2 Flow nozzle made for comparison   Nos 5–7 Lead tuyeres
C Graphite mold for casting lead tuyeres   ½ scale

pipe to the assembly shown in Fig 2   The 6-in. pipe has a baffle at the lower end to reduce eddy currents and turbulence in the air stream

The blowpipe and tuyere shown in Fig 2 were constructed of cast brass and brass tubing. The tuyere shown is a scale model of a standard American 6 by 12-in. tuyere. The blowpipe is also constructed to one-fifth scale and has a taper of ¼ in. per ft. as shown in Fig 2. Tuyeres 1 to 4 inclusive in Fig 1 were made of brass castings machined to the correct

contour.   Tuyeres 5, 6 and 7 were made of cast lead in a permanent mold, which is shown in Fig. 1C.

Fig. 1 shows a few of the tuyeres tried out.   About 30 tuyeres were constructed but they can be classified so that those in Fig. 1 represent all of the types.   The shapes of the air jets were not recorded for all the tuyeres.   Tuyeres of the same type gave very similar air streams and it was thought unnecessary to include any except those which showed quite
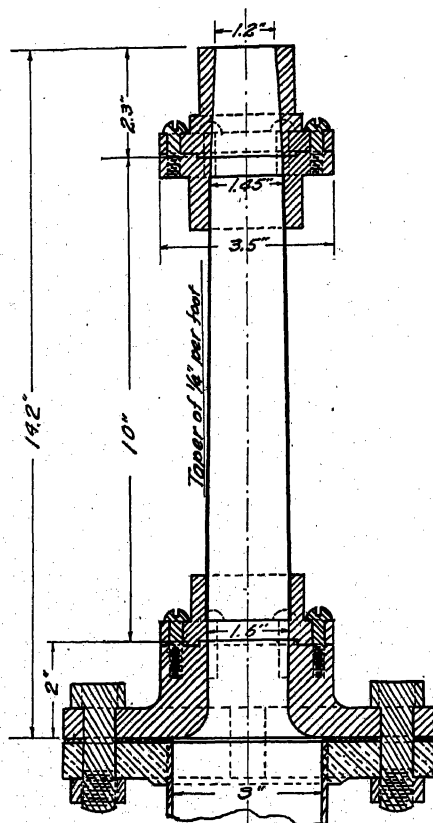
FIG. 2.—DETAIL OF BLOWPIPE AND TUYERE No. 1.

a difference in shape of air jet.   The tuyere shown in Fig. 1A is that shown in Blast Furnace and Steel Plant.   Tuyere No. 1 is a standard American tuyere, 6 by 12 in., of the converging type that is now most used.   The fixture shown in Fig. 1B was made to save time in making the tuyeres, as it did not require the machining of a flange on each tuyere.   Tuyere No. 2 was simply a flow nozzle or orifice with parallel walls and is not a model of any tuyere, but was constructed for comparison.   Tuyere No. 3 is a model of a tuyere proposed for use in some American plants.   In

this particular tuyere the angle of divergence is too great and the length of the diverging part of the tuyere is too short for efficient performance Tuyere No 4 is similar to tuyere 3, the difference being in the diameter of the throat   Tuyeres 5, 6 and 7 are some of the tuyeres which were made of lead, as previously described   The divergence shown on the drawing was found to give the best results   The length of the tuyere also varied the discharge and the shape of the air stream   An angle of more than 10° total gave an irregular air stream, because the air stream was unable to follow a divergence of more than 10°   For angles of divergence of less than 10°, the discharge fell off   It seems that for maximum air discharge, a diverging tuyere should have a divergence of 9° or 10° and a length of about four throat diameters

Besides the apparatus described, a Pitot tube was supported so that its position could be fixed at any point in the air stream.   Two vertical standards, parallel to the axis of the air stream, acted as a support for a carriage which could be moved up and down the standards   The carriage had an arm with a scale and vernier, so that the distance of the tip

TABLE 1.—*Effect of Tuyere Design on Air Discharged*

Air Discharged Is Expressed in Cubic Feet per Minute at 60° F , 14 65 Lb per Sq In Pressure and 50 Per Cent Saturation

Type of Tuyere	Air Discharged, Cu Ft per Min at Pressure of	
	1 5 In Hg	2 0 In Hg
No 1.—converging, 1 2 in dia at mouth	135	
No 4 —1 2 in dia at throat, ½ dia long, 15° divergence	162	
1 2 in dia at throat; ½ dia. long, 10° divergence	153	
1 2 in dia at throat; ½ dia long, 19° divergence	168	
1 2 in dia. at throat; 1 2 in long, 20° divergence	186	
No 2 —1 in dia at mouth, 1 dia long, straight	90	
No 3 —1 in dia at throat, ½ dia long, 20° divergence	125	
EFFECT OF LENGTH OF TUYERE ON VOLUME OF AIR DISCHARGED		
For 8° divergence, 1 in throat diameter		
2 in long	138	151
3 in long	152	175
4 in long	163	184
For 10° divergence, 1 in throat diameter		
No 5 —2 in long	142	163
No 6 3 in long	159	179
No 7.—4 in long	170	189
For 12° divergence, 1 in throat diameter		
2 in long.	147	170
3 in long	158	178
4 in long	165	184
Discharge for blowpipe only (without tuyere)	181	

of the Pitot tube from the axis of the jet could be determined The Pitot tube used was a streamlined impact tube designed by the Hydraulics Department of the University of Wisconsin Locations of points of equal total pressure (dynamic plus static) in the air stream were recorded for various planes across the air stream After an air stream had been surveyed as described above, the tops of the constant head curves were determined and the results plotted as shown in Fig 3. The impact tube was connected to one arm of a water manometer which was graduated in hundredths of a foot The pressure of the air in the air line was measured by means of a mercury manometer and was kept constant at 1 5 in Hg Since the air stream was symmetrical, it was necessary only to take data along one radius at any one plane for the plotting of the shape of the stream Readings were taken along radii at the mouth of the tuyere, 0 5 ft , 1 0 ft and 2 0 ft from the mouth respectively

The discharge of various types of tuyeres is given in Table 1, together with explanation of values Table 2 gives a typical record of the data obtained for most of the tuyeres used. The data in Table 2 are plotted as *B* in Fig 3. The data for the other curves of Fig 3 were obtained in the same manner Such data were obtained for most of the tuyeres

TABLE 2 —*Example of Data Taken July 9, 1929*

Barometric Pressure, 29 15 In Hg, Pressure of Air Held at 1 5 In Hg
Tuyere Used No 5, 1-in Throat, 2 In Long, 10° Divergence

Velocity Head Measured in Feet of Water Equivalent	Location of Position of Constant Air Velocity Heads				Distances from Tuyere Mouth Along Axis of Air Stream, Ft
	Distances from Center of Jet at Various Distances from Tuyere Mouth				
	0 5 Ft	1 0 Ft	1 5 Ft	2 0 Ft	
1 6					0 34
1 4					0 47
1 2	0 018				0 575
1 0	0 031				0 68
0 8	0 041				0 81
0 7	0 048				0 92
0 6	0 050	0 00			1 00
0 5	0 059	0 028			1 13
0 4	0 065	0 048			1 31
0 3	0 080	0 063	0 00		1 52
0 2	0 083	0 088	0 070		1 92
0 1	0 100	0 123	0 124	0 122	

Orifice Meter Data —Differential, 3 2 in water; absolute pressure, 31 65 in Hg, temperature, 107° F. Volume air at 60° F., 14 65 lb. per sq in pressure and 50 per cent saturation, is 148 cu ft per min

used in this work, but as the shapes of some of the air streams are very much alike only three of the plotted results are shown

As illustrated in Fig 1, in the diverging tuyere the angle of divergence and the length of the diverging portion were varied through a considerable range   The effect of varying the angle of divergence and the length of the
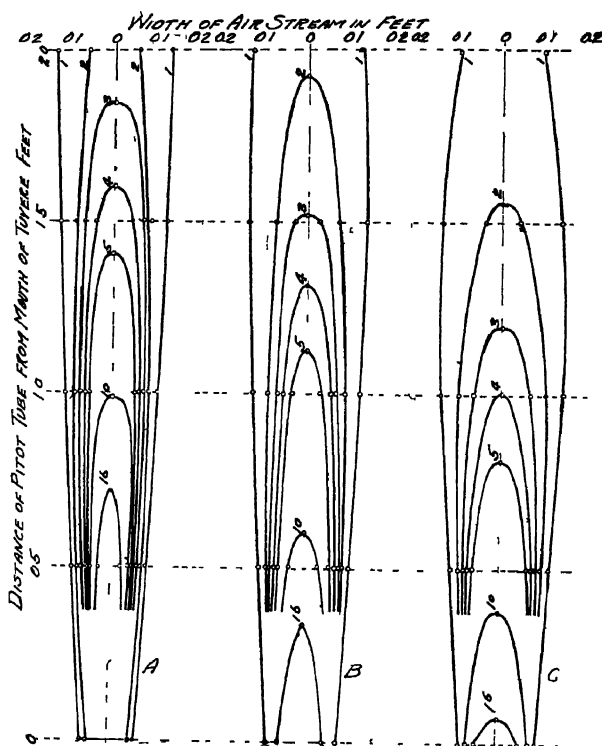
FIG 3 —ISOVELOCITY DIAGRAMS OF THREE AIR STREAMS
A   1 2-in converging tuyere; 136 cu ft per min , pressure 1 5 in Hg
B   1-in Venturi tuyere 2 in long, 10° divergence, 147 cu ft per min , pressure, 1 5 in Hg
C   1-in Venturi tuyere, 4 in long, 10° divergence, 170 cu ft per min ; pressure, 1 5 in Hg
Figures on curves denote velocity heads in tenths of a foot of water

diverging portion upon the volume of air discharged is shown in Table 1 The effect of changing the length of the tuyere is also shown graphically in Fig. 3, curves *B* and *C*.

In comparison of the graphs for the different tuyeres, the broadening of the air stream by a diverging type of tuyere is apparent.   The longer the diverging portion of a tuyere, the broader the air stream will become Increasing the angle of divergence increases the spreading effect also, but the effect falls off when an angle greater than 12° is used.   The diverging

tuyeres have considerably less linear velocity or head than those of the converging type, hence the penetrating power of a diverging tuyere is less than that of a converging type   A diverging tuyere is most efficient when the angle of divergence is between 9° and 10°   The 12° divergence gives a greater discharge for short tuyeres but does not give as great a discharge as a 10° diverging tuyere when the length is increased to four times the throat diameter

It is believed that the benefits derived from the use of a diverging tuyere are not due to the immediate shape of the air stream but are due to the distribution of the air in the furnace   Possibly an analogy would
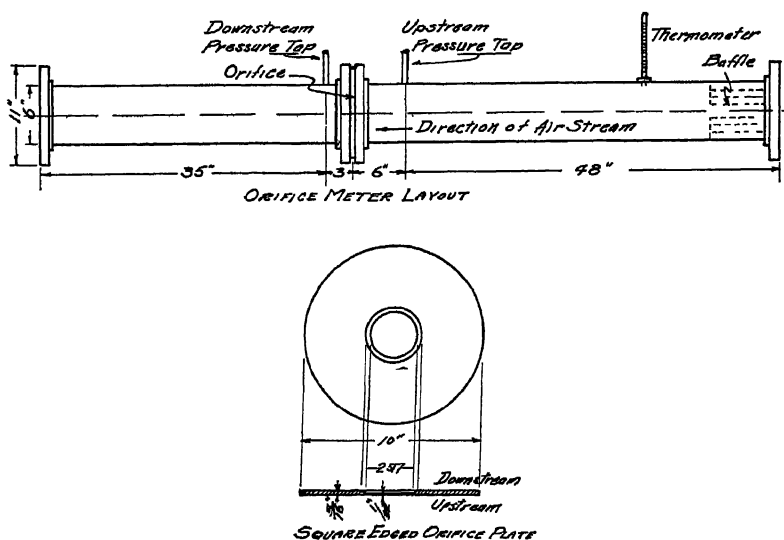
FIG 4.—DETAILS OF ORIFICE METER

Formula $V = NC_1'd^2\sqrt{\dfrac{p_1h(1 - 0\ 38w)}{458 + t}}$.   See text for development

$$V = 349\ 6\sqrt{\dfrac{ph}{458 + t}}$$

make this idea clearer.   Suppose a vertical tank were being filled with water at a constant rate, the water being introduced in a manner similar to the introduction of the blast in a blast furnace, the higher the velocity of the incoming water, the greater would be the turbulence of the water in the tank.   If Venturi nozzles were used, the turbulence would be at a minimum   It is believed that the same principle may apply to some extent in a blast furnace.

There are several methods for the measurement of air flow but none is as simple and inexpensive as the orifice method.   Then too, most of the air-measuring devices must be calibrated, while it has been shown that

for the orifice meter reasonable accuracy can be obtained by the careful construction of the orifice plate and equipment.

A diagram of the orifice meter as constructed is shown in Fig 4   The meter consisted of two lengths of 6-in pipe   The orifice plate was made of $3/16$-in brass plate, and machined as shown in the drawing   The upstream edge of the orifice was carefully machined, in order to have a sharp square edge   The downstream side was chamfered as shown   The location of the taps for the differential gage is also indicated.   The thermometer was placed in a well about six pipe diameters upstream from the orifice plate   A baffle was placed in the pipe, in order to reduce the eddy currents and the turbulence to a minimum   A mercury manometer was connected to the upstream pressure   The differential gage used to determine the pressure difference between the two sides of the orifice, or the pressure drop through it, was a water gage graduated in inches of water.

The theory of the meter is fully discussed in U. S Bureau of Standards *Research Paper* 49   The discharge coefficient given for this orifice as constructed and used in the location shown was found to be 0 608. Many factors enter into the discharge coefficient, such as the ratio of the diameter of the orifice to the diameter of the pipe and also the ratio of the upstream pressure to the downstream pressure.   The first ratio is constant for any given installation, while the second varied through such a small range under the conditions of this work that the coefficient did not vary appreciably from 0 608.   This coefficient is known as the discharge coefficient, based on the upstream static pressure with throat taps and approach factor included.   The general equation for air flow for this meter is given as

$$V = NC_1'd^2\sqrt{\frac{p_1h(1 - 0\ 38w)}{458 + t}}$$

where N is a constant for any one installation 129 4,

   C_1' is the discharge coefficient 0.608,

   d is the diameter of the orifice 2 517 inch,

   p_1 is the absolute upstream pressure in pounds per square inch,

   h is the differential in inches of water,

   $(1 - 0.38w)$ is the vapor fraction, being 0 9982 for 50 per cent. saturation,

   t is the temperature of the air in degrees Fahrenheit.

Applying the proper conversion factor to p_1 above and then expressing it as $p =$ inches of Hg, the evaluated formula becomes

$$V = 349.6\sqrt{\frac{ph}{458 + t}}$$

in cu. ft. per min at 60° F. and 14 65 lb. per sq. in pressure, 50 per cent saturation.

The Open-hearth Steel Process as a Problem in Chemical Kinetics

By Eric R. Jette,* New York, N Y

In order to control a chemical process by other than empirical, rule of thumb methods, two types of knowledge concerning the reactions involved must be available: (1) the thermodynamics of the reactions, and (2), by no means less important for efficient operation, the mechanisms and kinetics of the reactions

Information on the thermodynamic side enables the operator to decide upon initial and final conditions, whether heat must be added or removed from the system, whether the reactions proceed farthest in the desired direction at high pressure or low, etc. Knowledge of the mechanisms involves the determination of the individual steps by which an initial set of reactants, under given conditions, proceed to give the desired final products and kinetic studies upon which the mechanisms are based give the speed at which each of these reactions or steps take place. Thus thermodynamic studies of a reaction enable the operator to control the direction and extent to which the reaction can proceed, while kinetic studies enable him to control rates and thus the time efficiency of the operations The thermodynamics set the limit to which the reacting system approaches; the kinetics tell how fast the system actually approaches this limit The two types of information are complementary and not antagonistic even though in discussing the mechanism the introduction of thermodynamics is entirely needless and generally of no assistance, while in thermodynamic studies mechanism need not even be mentioned.

HETEROGENEOUS REACTIONS

The thermodynamic side of metallurgical reactions has received much attention in the past, the mechanisms, relatively, very little. The main reason for our present lack of information on the mechanisms of these reactions lies in the fact that every one of importance is a heterogeneous reaction; *i. e.*, the substances involved in the reaction exist in more than one phase, while, if we neglect the large amount of work which has been

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performed on certain surface reactions ("contact catalysis"), our most reliable experiments and theoretical investigations have been carried out in homogeneous systems

It will be well to consider briefly the nature of the difficulties arising in the theoretical treatment of heterogeneous reaction rates It is characteristic of these reactions that sooner or later a transfer of material (diffusion) across a boundary or interface between two phases becomes involved in determining the rate at which the process as a whole proceeds The chemical reaction may take place in both phases simultaneously, but it is entirely unlikely that it will proceed at the same rate in both. The total rate for the reaction in two phases becomes an extremely complex function of the time, because of the transfer back and forth of both reactants and products Even when the reaction takes place almost exclusively in one phase, the necessity for the transportation of substances across the phase boundaries is clear, because if the products of the reaction are not removed their concentrations increase and the reaction rate decreases, while a similar result is obtained if the reactants cannot diffuse into the phase rapidly enough for their concentrations to be maintained.

The rates of chemical reactions are governed by the law of mass action (see later); the rates of diffusion, for the cases which we shall consider, by Fick's first law (equation 16).   Neither of the two equations alone is at all complex, but because (1) both deal with rates, (2) the concentration of at least one substance in the reacting phase is influenced by both the chemical reactions and the diffusion process and (3) the concentration of this substance is generally not the one by which the rate of the process as a whole is experimentally measured, the combination of the two equations usually involves considerable indefiniteness as to the manner in which they should be combined and a long complex equation as the final result.   In dealing with mechanisms of heterogeneous reactions in any general way, a certain amount of mathematical manipulation is unavoidable, from the very nature of the problem.

It must not be forgotten that the equation resulting from such a combination is, in its way, a description of the process under consideration and at the same time carries along in it all the mathematical and otherwise simplifying assumptions which its author has found necessary to introduce.   Since it would be nonsensical to attempt to set up a perfectly general equation for a system in which an indefinite number of individual reactions and processes are taking place, it is evident that as a starting point we must have a clear cut and accurate description of all these individual reactions and processes.   The completeness of this qualitative description, as well as the accuracy by which each individual portion of it may be represented by a mathematical equation and the adequacy of the method by which the individual equations are combined,

all unite in determining the accuracy of the final result   Since the
systems in which the metallurgical reactions occur are nearly always
highly complex from a chemical point of view, it is absolutely essential
to scrutinize the final equation representing the rate of a process with
great care in regard to just what its author has included in it and particu-
larly in regard to those reactions and processes which have been omitted
deliberately or otherwise   Likewise, it is necessary to appreciate the
influence of the simplifying assumptions which may have been introduced
to reduce the final equation to a practicably workable form.

In the present article, the main purpose of which is stated in the
next section, the writer has proceeded to build up step by step an equation
which represents the rate of change of the FeO content of the metal with
time   While much of the argument leading up to this equation is given
in terms of the carbon oxidation, because this reaction proceeds more
slowly than the oxidation of the other elements present in the metal and
therefore largely determines the length of time the charge remains in
the furnace, the method of attack is suitable for the other elements as
well.   The more important differences between the oxidations of these
other elements and carbon are mentioned and there should be no great
difficulty in making the appropriate modifications   Every effort has
been made to state exactly what has been represented by each equation in
the development   In this way it is hoped that while in each succeeding
step the equation assumes a more fearsome appearance, this particular
discouragement to readers who are even less fond of complex mathemati-
cal functions than the writer will be somewhat mitigated by the verbal
information as to what may be expected of the equations as representa-
tions of the open-hearth steel process

INTRODUCTION TO THE OPEN-HEARTH PROBLEM

The importance of knowledge concerning the rates of chemical
reactions taking place in the open-hearth steel bath is obviously great,
but strangely enough the amount of literature on the subject, aside from a
few summaries of open-hearth heat data, is very small.   The two papers
on the rate of carbon oxidation by Feild[1] and the voluminous discussion
of the first of them are the most important contributions to date, although
Piérard's[2] critical discussion of an earlier paper by Feild[3] also contains
much material of theoretical importance   While Feild has been careful
in stating the assumptions leading to his general equation and those

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[1] A L Feild Rate of Carbon Elimination and Degree of Oxidation of the Metal
Bath in Basic Open-hearth Practice   Iron and Steel Tech in 1928, A I M E
(1928) 114, *Trans* A I. M E , Iron and Steel Div (1930) 23

[2] P Piérard: Discussion   *Rev de Mét* (1927) **24**, 47.

[3] A. L. Feild Physico-chemical Phenomena from Melt to Ingot   *Trans* Faraday
Soc. (1925) **21**, 255.

necessary for its application, there does not appear to have been given in these articles, or elsewhere, a discussion in more general terms regarding the adequacy of the description of the open-hearth process as represented by these equations, or of the implications involved in the assumptions which must be introduced in order that one may make any progress in the treatment of the subject from a theoretical point of view

In a complex group of chemical and physical processes such as constitutes the open-hearth steel process, certain individual processes may be treated theoretically with a high degree of exactness, others cannot It is obvious, but infrequently expressed, that one does not acquire exactness in a theoretical treatment merely by omitting the discussion of factors or processes which present knowledge does not permit us to discuss even from a theoretical standpoint   The final result of any theoretical treatment must, therefore, involve a certain amount of approximation which is carried along when the equations are applied to actual operations

Feild has discussed the rate of carbon elimination from the open-hearth bath   By taking into consideration two processes, the removal of FeO from the metal bath by chemical reaction with C, Si, Mn and P and the diffusion of the FeO from the slag to the metal, Feild finally obtains an equation which contains, as the principal variables, carbon concentration and time

This equation has been criticized by Styri[4] on the legitimate theoretical ground that it applies only to a "closed system" involving only the two processes mentioned above, while the open-hearth process actually is an "open system" with respect to these two processes; i e., the open-hearth process involves a number of other processes which also affect the rate of carbon elimination. Styri's objection brings up the question of how general an equation can be derived for the rate of oxidation of C, P, Mn, Si and S in the open-hearth process from the time the entire system is molten until the heat is tapped Such an equation, of course, is an ideal, and while keeping Styri's criticism in mind, Feild's equation is a valuable first approximation to the final solution

While it may be possible to set up such an ideal equation for the entire open-hearth process, the present writer is not at all certain that it would have any practical value   Furthermore, it is unlikely that such a general treatment will be forthcoming, in the near future, owing to the very serious difficulties imposed on the theoretical treatment by the complexity of the system and the lack of quantitative knowledge of many of the factors   More promising of results with significant practical applications is the less general and less exact method of studying the individual

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[4] H Styri. Discussion. *Trans.* A I M E (1930) 43

processes concerned and introducing them one by one into an equation which governs the concentration of dissolved oxygen in the metal bath. It is the dissolved oxygen whether in the form of FeO, MnO, or O_2 which, in the final analysis, determines the rate of elimination of C, Mn, Si, P or S by oxidation [5]

This is essentially what Feild has done and his work represents an important step in the understanding of the open-hearth process   On the other hand, such a treatment has certain serious limitations, which must be kept in mind when the resulting equation is applied to actual conditions   It is the purpose of the present paper to develop, even though a repetition of some of the work of earlier investigators is involved, step by step this method of approach to the open-hearth problem, indicating the assumptions which must be introduced in order to make progress   Incidental to this, and to emphasize the effect of the various assumptions, the physical process of diffusion will be discussed

LAW OF MASS ACTION

The well-known law of mass action states that for the reaction

$$aA + bB + cC + \qquad \rightleftarrows dD + eE +$$

we may write

$$-\frac{d[A]}{dt} = k_F[A]^a[B]^b[C]^c - k_B[D]^d[E]^e$$

in which the bracketed terms represent the total molecular concentrations of the individual substances in the reaction phase and k_F and k_B are the velocity constants of the forward and backward reactions   In order to apply this general equation to a chemical reaction, we must know not only the stoichiometric equation for the reaction but also its mechanism. The stoichiometric equation for the oxidation of carbon dissolved in molten iron is

$$C + FeO \rightleftarrows Fe + CO \qquad (A)$$

and this is also assumed to represent the mechanism of the reaction Direct experimental proof of this assumption is needed.

That the mechanism of the reaction is a matter of extreme importance for the theory of the open-hearth operation may be seen from the following considerations: As a matter of principle a series of consecutive chemical reactions cannot proceed faster than the slowest of the series. If the oxidation of carbon takes place by the pair of reactions

$$3Fe + C \rightleftarrows Fe_3C \qquad (B)$$
$$Fe_3C + FeO \rightleftarrows 4Fe + CO \qquad (C)$$

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[5] The elimination of S as MnS or FeS must be considered separately

and if the reaction (B) takes place much more slowly than (C), we get by application of the general equation

$$- \frac{d[C]}{dt} = k_F[Fe]^3[C] - k_B[Fe_3C]$$

and since [Fe] is constant

$$- \frac{d[C]}{td} = k'_F[C] - k_B[Fe_3C]$$

It then behaves as a pseudo-unimolecular reaction   This possibility cannot be eliminated on the ground that [Fe$_3$C] must be exceedingly minute, due to the possible dissociation of this compound at the elevated temperatures of the open-hearth bath   If this is the mechanism, the rate-governing factor is the carbon concentration and we would have no way of controlling the rate of carbon elimination other than by controlling the temperature and possibly the use of a "catalyst" for the reaction The FeO concentration would have nothing to do with the rate, except as pointed out later, in one peculiar case   If it should be the rate of formation of Fe$_3$C which determines the rate of oxidation of carbon, Feild's work as well as all that is to follow in the present paper may be discarded at once

If, however, the mechanism is through reactions (B) and (C) and (B) is more rapid than (C), we would be unable to distinguish between the mechanisms as expressed by reactions (A) and (C) by measurement of the reaction rate

The third possibility involving reactions (B) and (C) is that the individual rates are not far different   In such a case it would be possible to determine which process predominated if only the oxidation of Fe$_3$C was involved.   In the actual open hearth, especially in the early stages, silicon and phosphorus are also being oxidized by FeO and apparently at much higher rates than either C or Fe$_3$C   It is thus impossible to say whether (B) or (C) would determine the rate.   It might easily happen that the mechanism would change from one to the other during the course of the heat.   The temperature coefficients of the two reaction rates would probably be important factors in determining which of the two mechanisms predominates.

When reactions (B) and (C) have nearly the same rates but (B) is the slower, there is the theoretical possibility of exercising a certain amount of control of (B) through changing the rate of (C) by means of the FeO concentration.   According to velocity equation given above, the actual rate of carbon elimination is the difference between the forward and backward reaction rates   If reaction (C) is sufficiently slow so that for a given concentration of FeO the Fe$_3$C has an appreciable value at which a steady state exists between the two reactions, then any factor, such as the FeO concentration, which affects the forward velocity of (C) will affect

the steady state concentration of Fe₃C and thus affect the rate of carbon oxidation [6]   The more rapid (C) is with respect to (B) the lower is this steady state concentration and the more justifiable it becomes to neglect the backward reaction

A fourth possibility is that both carbon and Fe₃C are oxidized independently by FeO, but in this case it would probably be safe to ignore the Fe₃C oxidation on the ground of its extremely low concentration

We shall proceed, however, on the basis of the belief, although not of the certainty, that the mechanism of carbon oxidation is described by the chemical equation (A)   We may then write for the rate of reaction

$$-\frac{d[\mathrm{C}]}{dt} = k_F[\mathrm{FeO}]_U[\mathrm{C}] - k_B[\mathrm{CO}] \qquad [1]$$

assuming that [Fe] is essentially constant [7]

This equation means just what it states; i e , that if [C], [FeO]$_M$ and [CO] are known at a given moment and the velocity constants k_F and k_B have been determined for the existing temperature, we can calculate the number of gram molecules per unit volume of carbon oxidized in unit time at this moment   Nothing whatever is specified regarding the way in which the absolute values of [C], [FeO]$_M$ or [CO] are changing with time   Any one or all of them may be increasing, decreasing or remaining constant, depending entirely upon whether or not other processes exist in the system as a whole which supply or consume carbon, FeO and CO

We may differentiate this equation with respect to time, obtaining

after transposing and putting $\frac{k_b}{k_F} = m = equilibrium\ constant$

$$-\frac{d[\mathrm{FeO}]_M}{dt} = \frac{[\mathrm{FeO}]_M}{[\mathrm{C}]}\frac{d[\mathrm{C}]}{dt} + \frac{1}{k_F[\mathrm{C}]}\frac{d^2[\mathrm{C}]}{dt^2} - \frac{m}{[\mathrm{C}]}\frac{d[\mathrm{CO}]}{dt} \qquad [2]$$

With the difference that we must now know the rate of change of [CO] with time and the second derivative of [C], all the statements regarding equation 1 hold for equation 2   Both are complete or exact differentials.

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[6] The writer is indebted to Dr A B Kinzel for pointing out this possibility.

[7] In an article like the present one, the problem of nomenclature is always difficult   An attempt to gain clarity, somewhat at the expense of increased space, has been made by using the conventional chemical symbol for concentration and the most obvious possible subscripts wherever needed to indicate (1) in which phase the concentration indicated exists and (2) to what process the change of concentration or other quantity is due   Thus [FeO]$_M$ means the total molecular concentration of FeO dissolved in the molten metal and [FeO]$_S$ the total molecular concentration of FeO in the slag (not the "free" FeO)   The symbol $\left(\frac{d[\mathrm{FeO}]_M}{dt}\right)_{diff}$ means the change of total molecular concentration of FeO in the metal with time due to the diffusion of FeO from or into the slag.   Since the carbon as such is assumed to exist only in the metal, the subscript M will be omitted from the symbol [C]

When, however, we attempt to apply these equations to calculate the carbon or FeO concentrations or their rates of change at some time after the beginning of the reaction when the values $[FeO]_M$, $[C]$ and $[CO]$ were known, the exactness of the final equation depends upon the adequacy of the time functions of the other terms of the equation This is directly connected with the accuracy of our description of the system—ı e , whether the system is "open" or "closed"—for in general it is not possible to set up an exact equation for the behavior of a system which is incompletely described

In studying the open-hearth steel process, we are concerned with a system in which a certain concentration of carbon was present initially and the only possible cause for an increase of this concentration lies in the reversal of chemical reaction (A) The FeO concentration in the metal may be due to several factors which will later be considered separately

Carbon Oxidation without Outside Source of FeO

In this case, the simplest application of the mass-action law, there is a "closed" system consisting of a bath of molten iron in which C, FeO and CO are dissolved with the initial concentrations a, b and d respectively, the gas CO being at a definite pressure The concentrations of each of these substances at any moment is then given by $(a - z)$, $(b - z)$ and $(d + z)$ where z is the total change in concentration of carbon from the moment when $[C] = a$ and $t = 0$ Equation 1 then becomes·

$$- \frac{d[C]}{dt} = \frac{dz}{dt} = k_F(a - z)(b - z) - k_B(d + z) \qquad [3]$$

The simplifications of this equation where b is very large compared with z and $k_B (d + z)$ is small enough to be neglected, as well as the integrations of the resulting equations, may be found in textbooks of physical chemistry.[8]

From the stoichiometric equation (A), one molecule of FeO disappears from the metal bath for every molecule of carbon, so that in this case

$$- \frac{d[C]}{dt} = - \frac{d[FeO]_M}{dt} = \frac{dz}{dt}$$

The stoichiometric relation between FeO and C must also hold whether there is an outside source of FeO or not, and if we are careful to specify that the change in $[FeO]_M$ is due to the chemical reaction in the metal bath we may write

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[8] For example, H S Taylor: Treatise on Physical Chemistry, 866 et seq New York, 1924, Van Nostrand

$$-\left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{react}} = -\frac{d[\text{C}]}{dt} = k_F[\text{FeO}]_M[\text{C}] - k_B[\text{CO}] \qquad [4]$$

a relation which is just as exact as equation 1 and with the same values for k_F and k_B This expression will be used in a later section.

Carbon Oxidation When FeO Diffuses from Slag

By extending the system to include a layer of slag containing FeO as well as the substances and phases of the previous case, we have a system for which equations 1, 2 and 4 are still valid, while equation 3 is not We have another "closed" system but it is somewhat more complex Several methods of approach are possible

In this system the total amount of FeO, which cannot increase except by reversal of reaction (A), is distributed between the two liquid phases, but we shall assume that the interaction with carbon takes place only in the metal phase   The total rate of change of FeO in the metal phase is then the algebraic sum of the rate of removal by reaction with carbon and the rate at which it diffuses in from the slag   We have therefore:

$$\left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{total}} = \left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{react}} + \left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{diff}} \qquad [5]$$

where the subscripts "react." and "diff " refer to the reaction and diffusion processes   For the closed system in question this expression is also a complete differential, but this does not in the least imply that it is a complete differential for the actual open-hearth process.

For the diffusion process, according to Fick's law, we may write

$$\left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{diff}} = \frac{H}{v_M}\left([\text{FeO}]_S - \frac{[\text{FeO}]_M}{r}\right) \qquad [6]$$

The subscript S refers to slag, v_M is the volume of metal, $r = [\text{FeO}]_M/[\text{FeO}]_S$ is the distribution coefficient of FeO, and H is a coefficient for the diffusion of FeO   The distribution coefficient is involved because when there is equilibrium between FeO in the two phases equation 6 must be equated to zero; the value of $[\text{FeO}]_S$ is the total concentration of FeO in the slag and not the "free" or "effective" FeO H is not the true diffusion coefficient but will be considered as constant for the time being.   It will be defined exactly later, in equation 19.   It may be noted that nothing is specified at this point regarding either $[\text{FeO}]_S$ or $[\text{FeO}]_M$ as functions of time.

We may now proceed over either of two paths.   It has been shown that $\frac{d[\text{C}]}{dt} = \left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{react}}$; we may substitute this and equation 6 in equation 5 and the result in equation 2   The value of $[\text{FeO}]_M$ may be

found by transforming equation 1 and inserting into this equation. The final result is

$$-\frac{d[C]}{dt} - \frac{H}{v_M}[FeO]_S - \frac{H}{v_M r k_F[C]}\frac{d[C]}{dt} + \frac{Hm[CO]}{r v_M[C]} + \frac{1}{k_F[C]^2}\left(\frac{d[C]}{dt}\right)^2$$

$$- \frac{m[CO]}{[C]^2}\frac{d[C]}{dt} - \frac{1}{k_F[C]}\frac{d^2[C]}{dt^2} + \frac{m}{[C]}\frac{d[CO]}{dt} = 0 \quad [7]$$

This equation is almost identical with equation 7 of Feild's first paper and modified in his second [9] The differences between this equation and Feild's are (1) differences in nomenclature, (2) the absence of the quantity p, since we have not taken the oxidation of Si, P and Mn into consideration, (3) the presence of the term $1/v_M$ which is necessary when the slag and metal volumes are not equal and (4) the final term on the left which Feild omitted, probably inadvertently, when listing the corrections in his second paper Not only is this equation essentially the same as Feild's, but the method of obtaining it is identical.

The second approach to the problem is to substitute equations 4 and 6 into 5, which yields.

$$\left(\frac{d[FeO]_M}{dt}\right)_{total} = \frac{H}{v_M}[FeO]_S - \frac{H[FeO]_M}{v_M r} - k_F[FeO]_M[C] + k_B[CO]$$

Upon differentiating this equation with respect to time and transposing, we get:

$$-\frac{d[C]}{dt} = \left(\frac{H}{r k_F v_M} + [C]\right)\left(\frac{d\ln[FeO]_M}{dt}\right)_{total} + \frac{1}{k_F[FeO]_M}\left(\frac{d^2[FeO]_M}{dt^2}\right)_{total}$$

$$- \frac{H}{k_F[FeO]_M v_M}\frac{d[FeO]_S}{dt} - \frac{m}{[FeO]_M}\frac{d[CO]}{dt} \quad [8]$$

A third approach is to modify the $(b - z)$ term in equation 3 to include the diffusion process The concentration of FeO in the metal in this case is equal to b, the original concentration at $t = t_1$ plus the amount which has diffused in during the time interval in question, less the amount removed by the reaction. The increase in concentration due to diffusion is given by

$$\int_{t_1}^{t_2}\left(\frac{d[FeO]_M}{dt}\right)_{diff} dt$$

Instead of writing the momentary concentration of FeO in the metal equal to $(b - z)$, as was possible for the homogeneous isolated system, we must now write

$$[FeO]_M = b - z + \int_{t_1}^{t_2}\left(\frac{d[FeO]_M}{dt}\right)_{diff} dt \quad [9]$$

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[9] A. L. Feild. References of footnote 1, pp 122 and 26.

The lower limit of the integration is the time the value of $[FeO]_M$ was

b The rate of removal of carbon in this case is given by

$$-\frac{d[C]}{dt} = k_F(a - z)\left(b - z + \int_{t_1}^{t_2}\left(\frac{d[FeO]_M}{dt}\right)_{diff} dt\right) - k_B(d + z) \quad [10]$$

Since for this system, the rate of diffusion is given by equation 6, we obtain

$$-\frac{d[C]}{dt} = k_F(a - z)\left(b - z + \int_{t_1}^{t_2}\frac{H}{v_M}\left([FeO]_s - \frac{[FeO]_M}{r}\right)dt\right) - k_B(d + z) \quad [11]$$

Discussion of Equations 7, 8 and 11

The three equations 7, 8 and 11 are, of course, merely three different ways of representing the given situation   When applied to the open-hearth process, none of them can be expected to reproduce the rate of carbon elimination with any greater accuracy than the simple conception of the process, as outlined in the preceding section, describes the whole of the open-hearth process

While in the treatment described above, as in Feild's, the final equations deduced have been written so as to give the rate of carbon oxidation, our chief concern really has been the concentration of FeO in the metal This is the only logical method, provided, of course, that the rate-determining reaction is given by reaction (A) or (C) and not by (B)   The control of the momentary concentration of FeO in the metal represents the only way of controlling the rate of carbon oxidation available to the open-hearth operator apart from the obvious factor of temperature Of the various processes that may affect the FeO concentration in the metal, it must again be emphasized that only two have been considered in obtaining equations 7, 8 and 11   The relative importance of rate of reduction of FeO by carbon and of diffusion of FeO from a slag in comparison with the other processes which affect the value of $[FeO]_M$ can be decided only by experience in the open-hearth practice and by laboratory experiments in which the individual processes can be studied with some degree of accuracy and of independence from other processes

Feild has carried the quantitative application of equation 7 about as far as existing published data justify   Quantitative data suitable for discussing equations 8 and 11 have not appeared   A qualitative discussion of several hypothetical cases seems to the writer to be of considerable importance since it indicates certain points which may prove to be of practical interest   For such qualitative discussion, equation 11 or 10 seems to be more suitable than either 7 or 8

CASE I.   *FeO in metal in equilibrium with slag at start; rate of diffusion greater than rate of reaction; backward reaction negligible* —In this case the metal remains saturated with FeO, i. e , it is in equilibrium with the slag, throughout the entire course of the reaction and b represents the initial

equilibrium concentration   Due to the decrease of $[FeO]_S$ during the reaction the term under the integral sign in equations 10 and 11 is somewhat less than z but after the initial rapid decrease in carbon content we may consider as a first approximation $[FeO]_M$ = constant   We have then a pseudo-unimolecular reaction[10] for which the mass-action equation 1 simplifies to

$$-\frac{d[C]}{dt} = k'[FeO]_M[C] = k''[C]$$

and

$$-\frac{1}{[C]}\frac{d[C]}{dt} = -\frac{dln[C]}{dt} = k'r[FeO]_s = k'' \qquad [12]$$

Because of the decrease of $[FeO]_s$ during the reaction the actual rate of carbon elimination would be somewhat slower than if $[FeO]_s$ were constant   To maintain this quantity constant would, however, necessitate the introduction of another process ("opening the system"), such as ore addition or direct oxidation of metal

It is also possible to modify the system in such a way that the change in $[FeO]_s$ is small in comparison with the total concentration, in which case the term containing $[FeO]_s$ in equations 7 and 11 would be constant

De Loisy[11] obtains exactly the same form of equation as this by assuming that the reaction takes place at the interface between metal and slag   Consequences of this assumption are that the FeO content of the slag at all times is constant at the interface and that the slag layer is stirred violently by the gaseous CO formed at the interface while the metal bath remains quiescent   In such a case, it is the rate of diffusion of carbon in the metal that determines the reaction rate   The experimental results quoted agree very well with the equation for a monomolecular reaction, and possibly no clearer example could be found to illustrate the facts that the same set of data can be used to establish two almost diametrically opposed mechanisms and that an equation which expresses the results of a given set of experiments is not in itself proof of the mechanism unless the other possibilities have been eliminated by careful and controlled variation of the experimental conditions   This situation will exist until data on both $[C]$ and $[FeO]_M$ at constant temperatures and over a considerable range of conditions becomes available

CASE II   *Initial concentration of FeO in metal is high; initial rate of diffusion less than initial rate of reaction; backward reaction negligible.*—
In this case the value of the term under the integral sign in equation 11 is less than z during the first stages, and during these stages of the reaction the FeO content of the metal will decrease, but not as rapidly as if the

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[10] H Styri Theory and Practice of Steel Refining *Jnl* Iron and Steel Inst (1923) **108**, 217

[11] E de Loisy Sur la vitesse d'élimination du carbone au four Martin *Rev de Mét.* (1926) **23**, 369.

diffusion process did not exist. The rate of diffusion is increasing during this stage However, as the value of $[FeO]_M$ approaches $r[FeO]_s$ the rate of diffusion must decrease and hence during the heat the diffusion rate passes through a maximum Finally, as the carbon content approaches equilibrium with the limiting FeO concentration, i e, $[FeO]_M = r[FeO]_s$, the diffusion rate approaches zero This case is represented by the purely hypothetical diagram in Fig. 1

The rate of carbon oxidation decreases continuously from the beginning of the reaction, approaching zero as equilibrium is approached Depending upon the value of the reaction velocity constant, the curves of the rate of carbon oxidation against time and of rate of diffusion against time may or may not intersect. If the former, we cannot say from present data whether the intersection will be on the rising or descending side of the maximum in the diffusion-rate curve Whether the two curves intersect or not, both must approach zero together, at least towards the
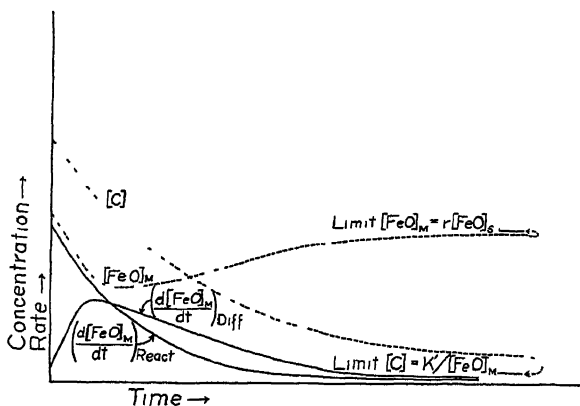
FIG 1.—HYPOTHETICAL DIAGRAM, CASE II.

end of the reaction as the system reaches equilibrium, for as long as the rate of carbon oxidation has a finite positive value the rate of diffusion must also be finite and positive

If there is an intersection on the descending portion of the diffusion-rate curve there is a possibility that the two rate-time curves coincide beyond the intersection. This would mean that the rate of diffusion equals the rate of reaction and therefore a steady state would exist between the two opposing processes. In such a steady state $[FeO]_M$ is constant and equation 12 is applicable. However, the carbon content is continuously decreasing and with it the rate of FeO reduction also decreases; this in turn means that the rate of diffusion must decrease. In terms of equation 6 this would demand that either the difference $\left([FeO]_s - \dfrac{[FeO]_M}{r}\right)$ or H decreases. Since $[FeO]_{M,}$ and presumably

$[FeO]_M/r$, is constant, this would mean that $[FeO]_s$ decreases, which is possible in the closed system under consideration   In actual open-hearth operations it seems less likely to occur since $[FeO]_s$ generally increases due to other factors.   A decrease in H depends upon certain physical and mechanical conditions which will be discussed in a subsequent section While such a situation may be possible, the writer does not believe that the hypothesis of a steady state will lead to results of importance as far as practice is concerned   In view of what is to be discussed in a subsequent section, it will be noted that a steady state with respect to $[FeO]_M$ will lead to decreasing values of the product $[FeO]_M[C]$, due to the continuing carbon oxidation, but it is obvious that this is not the only condition that would give such a result

CASE III   *Rate of reaction much higher than rate of diffusion during entire course of the process* —The product $[FeO]_M[C]$ under these circumstances is essentially the equilibrium value but exceeding this value by a trifling amount else the reaction could not proceed in the forward direction.   Since the carbon cannot be eliminated faster than excess FeO is supplied from the slag, the rate of elimination is governed by the diffusion process and equation 6 is equal to $-\dfrac{d[C]}{dt}$ As the value of $[FeO]_M$ must then be small, the term $[FeO]_M/r$ is negligible in comparison with $[FeO]_s$ Hence the rate of carbon oxidation would be constant in so far as the product $\dfrac{H}{v_M}[FeO]_s$ is constant and the reaction would appear to be of the "zero" order in this case; *i. e ,* independent of both $[FeO]_M$ and $[C]$ Since by equation 1 the rate of carbon oxidation is given by $k_F[FeO]_M[C]$ if the backward reaction may be neglected, we are able to calculate k_F by knowing the value of $[FeO]_M[C]$ from a direct determination, or H by knowing $[FeO]_s$ and v_M.   For this special case the relations would be

$$- \frac{d[C]}{dt} = \text{const} = \frac{H}{v_M}[FeO]_s = k_F[FeO]_M[C] = k_F K_{eq}$$

CASE IV.—Other combinations of the conditions in the headings of Cases I and II will readily suggest themselves, but here we shall mention only the effect of increasing concentration or partial pressure of CO within the metal.   This has been considered as a possibility towards the end of an open-hearth heat, as the reaction becomes very slow and the bath becomes "flat."[12]   It follows immediately from the equilibrium law that the product of the concentrations of FeO and carbon in the metal must be higher at high pressures of CO than at low.   According to equations 8 and 11, the rate of carbon elimination decreases if [CO] increases, since

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[12] A L Feild Second reference of footnote 1.

the system is thereby brought closer to the equilibrium point   However, the irreversible diffusion process is still going on building up the FeO concentration in the metal   Whether equilibrium will result depends upon the relative velocity of diffusion plus that of the backward reaction, both of which increase the FeO content and the velocity of the forward reaction which reduces it   The fact that values of the product $[FeO]_M[C]$ higher than the equilibrium value are obtained is not in itself a proof that the CO content of the metal is greater than corresponds to one atmosphere pressure, as will be clear from the next section.

So-called "Practical Equilibrium" in the Open Hearth

Experience in some open-hearth heats has shown that over a considerable portion of the open-hearth process the product

$$[C][FeO]_M = \text{constant} = K' \qquad [13]$$

For the reaction $C + FeO \rightleftarrows Fe + CO$ the equilibrium expression is

$$K_{eq} = \frac{[Fe][CO]}{[FeO]_M[C]} \qquad [14]$$

which, since [Fe] is constant and [CO] may be put equal to 1 atm for most purposes, easily reverts to equation 13   Prior to the work of Kinzel and Egan,[13] who determined the value of K' to be 0 0005 at 1550°, the concentrations being expressed in weight per cent , and [CO] = 1 atm, it was considered that the constancy of the value of the product, approximately 0 01 (Herty), indicated that equilibrium between the carbon and FeO dissolved in the metal existed at all times during the operation.   The essential difference in the conditions under which these two widely different values were obtained is that Kinzel and Egan had no slag present, while all the other values were found for metal melted under slags   In order to reconcile the two values, it has been suggested[14] that at the end of the open-hearth process the concentration of CO dissolved in the metal increased to a value corresponding to external pressures of 20 to 25 atmospheres.

It is interesting to inquire in what manner a constant value of the product much higher than Kinzel and Egan's value could be obtained without introducing such an assumption of equilibrium under high pressures of CO.   To maintain a constant value of the product the following condition must be maintained: At a given arbitrarily chosen moment let

[13] A. B Kinzel and J J Egan. Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron. *Trans A I. M E* , Iron and Steel Div (1929) 304

[14] J M Gaines, Jr : Discussion   *Trans A. I M E.* (1929) 253. See, however, J Johnston *Ibid* , 259.

the concentrations of FeO and carbon be $[FeO]_{oM}$ and $[C]_o$ Their product is the value of K'' To maintain this value constant we must have

$$\left([FeO]_{oM} + \left(\frac{d[FeO]_M}{dt}\right)_{total}\Delta t\right)\left([C]_o + \frac{d[C]}{dt}\Delta t\right) = K'' \qquad [15]$$

where Δt is the time interval between the initial moment and some other time   By multiplying out, neglecting the term containing the product of the two differential coefficients and rearranging, we obtain

$$\frac{1}{[C]_o}\frac{d[C]}{dt} = -\frac{1}{[FeO]_{oM}}\left(\frac{d[FeO]_M}{dt}\right)_{total}$$

If the value of $\left(\dfrac{d[FeO]_M}{dt}\right)_{total}$ thus obtained is substituted in equation 5 and recalling that $\dfrac{d[C]}{dt} = \left(\dfrac{d[FeO]_M}{dt}\right)_{react}$ the result is

$$\left(\frac{d[FeO]_M}{dt}\right)_{diff} = -\left(1 + \frac{[FeO]_{oM}}{[C]_o}\right)\frac{d[C]}{dt} \qquad [15a]$$

According to this equation, if the initial time is chosen at a period where the ratio of the two concentrations is low (e. g. $[C]_o$ is high) the diffusion process needs only to supply the metal bath a little more than one concentration unit of FeO for each unit of carbon oxidized   At higher ratios the diffusion rate must be relatively more rapid   In Figs. 2 and 3 of an article by Herty, Gaines, Freeman and Lightner,[15] data were presented which showed that as the carbon content decreased, the FeO content of the metal increased which, of course, is possible only if the rate of diffusion of FeO into the metal is more rapid than its reduction by carbon   At the end of the basic heat in Fig. 2 and prior to deoxidation of the acid heat in Fig 3, there is in each case a period of approximately ½ hr during which three samples were taken and analyses made.   In the basic heat the value of the product is about 0 022 and in the acid heat about 0.024, the concentrations being expressed in weight per cent.[16]   The value of the ratio $[FeO]_{oM}/[C]_o$ is nearly unity in both cases, which means that the diffusion process supplied 0 02 per cent FeO to the metal for every 0 01 per cent. C oxidized.   It is obvious that other processes occur in the open-hearth steel bath which influence the concentration of FeO in the metal and such processes will be considered in subsequent sections. It may be necessary, therefore, in any actual cases, to substitute for the right-hand side of equation 15a a suitably modified term which will include all these other processes

[15] C H. Herty, Jr , J M Gaines, Jr , H Freeman and M. W Lightner A New Method for Determining Iron Oxide in Liquid Steel   *Trans* A I M E , Iron and Steel Div (1930) 28

[16] Equation 15a in terms of weight per cent. may be derived in the same manner as above and results in the same form of expression

It may be observed at this point that nothing whatever has been specified regarding the actual value of K'' and it is particularly to be emphasized that it stands in no direct relationship with equilibrium constant   The argument advanced in the above paragraphs is thus quite independent of any specific value of K' such as Kinzel and Egan's 5×10^{-4}. It follows naturally, however, that if the carbon and FeO of the metal bath in the heterogeneous metal-slag system under consideration are actually in equilibrium, or as near to it as the rate of the irreversible diffusion process permits, the conditions demanded by equations 15 and 15a are automatically fulfilled   It seems clear, however, that from analyses of the metal bath in actual open-hearth conditions the product of $[FeO]_M$ and $[C]$ yields directly K'' and not K'. Further, since the constancy of K'' must be demonstrated by actual analysis, it is even unnecessary to demand that the temperature be unvarying during the period when K'' shows little or no change, in this respect it is quite different from K' That the two values are equal—i e , equilibrium exists—must be demonstrated independently, and for this purpose two methods are available: (1) Under special conditions it may be possible to conduct the reaction in the open-hearth furnace in a reversible manner, so that the same value of the product will be approached from the low side as well as the high side, and this in turn may be secured either by variations in temperature or by starting under conditions such that the backward course of reaction (A) predominates, (2) by comparison of the value of K'' with the value of K', which has been determined under rigorous equilibrium conditions   The writer's present tendency to accept the value of 5×10^{-4} for K' rests on the fact that it resulted from a serious attempt to secure equilibrium between FeO and C in the absence of any slag as well as the excellent agreement between this value and the thermodynamical calculations of Styri and of Gaines [17]   It is recognized, of course, that the objection raised by Larson[18] concerning the possibility of retaining the equilibrium concentrations during the period the metal was cooled through the freezing point is yet to be answered in a finally conclusive manner.

It is, however, anything but clear to the writer why a condition satisfying equation 15a should ever occur in the actual operation of the open-hearth furnace and even less clear why in such a complex system it should persist long enough to permit the at least apparently justifiable assumption that equilibrium has been established   Since the data on which the

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[17] H Styri Op cit , footnote 10.

  J M. Gaines, Jr Discussion   Trans A I M E , Iron and Steel Div. (1929) 312

  H Styri· Ibid , 314

  [18] B M. Larsen Origin and Effect of Inclusions in Steel. Metals & Alloys (1930) 1, 713

high values were based were at best rather meager in extent, and some of the assumptions introduced by no means unobjectionable, it may be suggested that the so-called "practical" constant is largely illusory and more extensive quantitative data would eliminate it entirely   In addition, it may be observed that within the present limits of error of sampling and of analysis for carbon and FeO, especially the last, the actual behavior may be rather far different from that described by equation 15a and yet the value of the product $[FeO]_M[C]$ appear to be sensibly constant   The writer concludes that if the high values frequently obtained are real, and, therefore, must be explained, the kinetic interpretation given above is preferable to either of the following alternatives:

(a). Equilibrium between carbon and FeO exists throughout the entire course of the reaction and value of $K' = 0\ 0005$ is wrong.

(b). The value of $K' = 0\ 0005$ is correct but the concentration of CO corresponds to from 20 or more atmospheres external pressure with equilibrium existing at all times.

Another conclusion, which would follow from the above, is that the average open-hearth heat is tapped a considerable time before the FeO of the metal is in equilibrium with the slag and before the carbon is in equilibrium with the dissolved FeO.   It will also be seen that even at [CO] corresponding to one atmosphere pressure, "overoxidation," i e., the presence of more FeO in the metal than necessary to satisfy $[FeO]_M$-$[C] = K'$ at the existing value of [C], is inevitable and that the amount of "overoxidation" depends on the FeO content of the slag, the distribution constant r, the time required for the last stages of carbon oxidation as well as the carbon content and temperature.   Finally, because of the unidirectional nature of the diffusion process, the longer the steel remains in the furnace after deoxidizing agents have been added, the greater the FeO concentration of the metal, since under this condition it follows from equation 6 that the diffusion rate will be high.[19]

It may be noted that at constant [CO] a constancy of $[FeO]_M[C]$ means a constant rate of carbon oxidation.   This is the linear carbon-time curve which Feild[20] reports having observed and which he assumed in his subsequent calculations   Since the value of the equilibrium constant found by Kinzel and Egan is so small, we may disregard the backward reaction without much danger of error   On the basis of this assumption, it is possible to write for such favorable cases as Feild has noted simply

$$- \frac{d[C]}{dt} = k_F[\dot{F}eO]_M[C] = \text{const}$$

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[19] C H Herty, Jr : Diffusion of Iron Oxide from Slag to Metal in the Open-hearth Process.   *Trans* A. I. M E , Iron and Steel Div (1929) 299.

   H Styri: *Op. cit* , footnote 10

[20] A. L. Feild: First reference of footnote 1, 127.

Thus if the carbon-time curve is known, and linear and the $[FeO]_M$ and $[C]$ have been actually determined by analysis for the corresponding period, we have here a method of determining the velocity constant k_F It is to be observed that it is unnecessary in this case to specify the processes that govern the value of $[FeO]_M$ because the equation contains only the momentary value of this quantity which must be determined by direct methods

The reaction would appear to be of the "zero" order similar to Case III but the implications involved in the two must not be confused   In Case III the FeO in the metal is essentially in equilibrium with the carbon but not with the FeO of the slag   The method of calculating k_F as outlined above does not depend on assumptions as to equilibrium of any sort existing between FeO in the metal either with the carbon or the FeO in the slag, but merely on an experimental demonstration that $d[C]/dt$ is constant and $[FeO]_M[C]$ is constant   The distinction between the two cases lies in whether the value of the product is that corresponding to equilibrium or not

Other Chemical Reactions in the Metal Bath

Among the chemical reactions which thus far have been omitted for the sake of simplification, there are the oxidations of Mn, P and Si dissolved in molten iron   The chemical equations for these reactions are respectively:

$$Mn + \ FeO \rightleftarrows Fe + MnO \tag{D}$$
$$2P + 3FeO \rightleftarrows 2Fe + P_2O_3 \tag{E}$$
or $$2P + 5FeO \rightleftarrows 5Fe + P_2O_5$$
$$Si + 2FeO \rightleftarrows SiO_2 + 2Fe \tag{F}$$
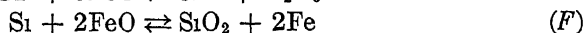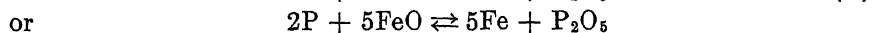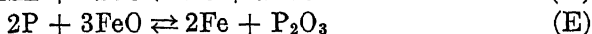
The important question of whether these equations actually represent the mechanism is again involved   The last reaction apparently takes place with great rapidity, reaching equilibrium in a very short time [21] The others also seem to be rapid in comparison with the carbon oxidation during the working period   In passing, however, it may be mentioned that the heats of these reactions and the heats of formation of these oxides give no basis for judging the relative rates of the reactions   There is no known relation between heats of reactions and velocities with which the reactions take place

Sandelin,[22] in a recent article, gives the results of investigations of three acid open-hearth heats prior to the beginning of the boil. He finds that the rate of oxidation of Si and Mn under these conditions is expressed

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[21] J L Keats and C H Herty, Jr Elimination of Metalloids in the Basic Open-hearth Process *Trans* A I M E (1926) **73**, 1080, Fig 1

[22] Sandelin *Jernkontorets Ann* (1929) **84**, 519

by the equation for a monomolecular reaction, i e, of the same form as equation 12 This result was obtained in spite of the fact that in one heat the FeO content of the slag increased, in the second decreased and in the third remained essentially constant On this basis he concluded that the rate of diffusion of FeO from the very fluid slags used in these heats was sufficiently rapid to maintain a constant value of $[FeO]_M$ and equilibrium distribution of FeO between slag and metal While the plot of log [Si] and log [Mn] against time for his third set of data are excellent straight lines, it must be emphasized that the author's interpretation of these results depends on the assumption that reactions (D) and (F) express the mechanisms of Si and Mn oxidation, a fact which is yet to be demonstrated

In the case of silicon, it is possible to account for these results by a mechanism analogous to reactions (B) and (C), the formula for the compound probably being FeSi This mechanism in the case of silicon may be complicated, however, by the formation of double carbides of iron and silicon In the absence of definite proof that the FeO or oxygen content of the metal was constant during the period investigated, since the requisite analyses were not made, such mechanisms may not be summarily disregarded

For manganese it is somewhat more difficult to conceive of plausible mechanisms, other than the one Sandelin himself has advanced, which would yield an equation for a monomolecular reaction Due to the fact that the carbon content changed very slightly during the periods reported, the further possibility that the manganese oxidation rate is controlled by the rate of formation of a manganese carbide is not entirely ruled out. In the opinion of the present writer, however, these data give strong support to the mechanism represented by reaction (D) But it must be cautioned that the manganese case does not give support for reaction (F) as the mechanism of the silicon oxidation There is nothing inconsistent in considering reaction (D) as determining the rate of manganese oxidation, thereby indicating a constancy of $[FeO]_M$ and the rate of formation of FeSi as the rate determining factors in the silicon oxidation, since the latter is independent of $[FeO]_M$

In so far as the mechanisms of manganese and silicon oxidation are given by reactions (D) and (F) the rate equation will be analogous to equation 1 with the exception that for silicon the term $[FeO]_M$ appears as the square.   This would make the silicon oxidation obey a trimolecular law.   The infrequency with which genuinely trimolecular reactions occur in the field of chemical kinetics, together with the known rapidity with which silicon is oxidized in the open-hearth bath, would lead one to suspect that the actual oxidation takes place by a rather different mechanism.   The same argument would apply to reaction (E) as the mechanism of phosphorus oxidation.   The importance of the backward reactions in

equations (D), (E) and (F) is difficult to estimate   Like CO, each of the resulting oxides has a certain solubility in iron, although probably only that of MnO would be numerically significant.   Each of these oxides and FeO have the tendency to intercombine to form silicate and phosphates and, at least in the case of MnO, it would be necessary to consider the distribution of the oxide between metal and slag   However, sufficient has been given in the preceding portion of the article to indicate a method of approach in interpreting the data when finally they are secured, and the factors that must be taken into account in the theoretical treatment of the reactions taking place in the metal bath

In the absence of quantitative information over a longer period of the heat sufficient to discuss the manganese, silicon and phosphorus cases individually, the manner in which Feild has treated the situation is as good as any   Feild takes all three reactions into account by the term p, which is simply the ratio of the total rate of FeO consumption (the sum of the rates for C, Mn, Si and P) to the rate of consumption by carbon alone.   The quantity p is thus a function of time   Further discussion does not seem necessary

Of the reactions involving substances contained in the slag layer the two of greatest importance are the oxidation of FeO to Fe_2O_3 at the slag-gas interface and the reduction of the higher oxide at the metal-slag interface   Again insufficient data are available to discuss the relative importance of these two processes   The second of the two reactions may be very effective in increasing the FeO content of the metal   As far as the reaction of Fe_2O_3 dissolved in the slag with Fe at the metal interface is concerned, the process may presumably be considered as the result of a diffusion process transporting the oxide to the interface followed by a rapid reaction with the iron   The theoretical treatment and experimental verification of this type of process has already been given by Nernst, Brunner, Noyes and Whitney, Edgar, van Name and others and is summarized by Taylor,[23] so that discussion need not be given here

In the cases that have been studied the product of the reaction was soluble only in the phase carrying the oxidizing or dissolving agent   In the open-hearth system, FeO is soluble in both phases and it is impossible to say from existing data in what proportion the FeO produced is distributed between metal and slag   The relative rates of solution of FeO in the two phases depend upon the concentration of FeO in metal and slag in the immediate vicinity of the interface, besides certain constants characteristic of the two solution processes.   The convention, adopted by Feild as well as Herty, in determining the "effective FeO," of taking the sum of the FeO and 1 35 times the Fe_2O_3, while a matter of necessity at the present, is not satisfactory from the kinetic standpoint because it definitely

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assumes that all the FeO produced by the reduction remains in the slag and reaches the metal only by the diffusion process possibly influenced by high local concentrations. If all of the factors involved in the reaction at the interface were known, it would be possible to take into account the effect of this reaction upon the FeO content of the metal, by an additional term in equation 5 Since the percentage of Fe_2O_3 in the slag may be one-quarter or even greater proportion of the FeO percentage, and since each molecule of Fe_2O_3 by reaction yields 3FeO, this is evidently a process that cannot be neglected in the kinetic analysis

Another group of processes is involved in the effects of mechanical additions of solid ore to the bath Here rate of melting and rate of solution in the slag, as well as the rates of solution of melted ore in the metal, must be considered While practical experience shows that the rate of carbon elimination is high in the part of the bath where ore has been added, the writer sees no way of approaching this situation from a theoretical standpoint

The kinetic treatment of the processes during the "lime boil" seems quite impossible at the present time While it is certain that some of the individual processes could be discussed in considerable detail, these items do not seem to form important parts of the whole. The particular factors that lead the writer to omitting the consideration of any of the processes characteristic of this period are the rapid variation of physical conditions, especially temperature, and the lack of any legitimate and useful method of approach to the problem of limestone decomposition rate in the furnace. The actual rates observed as measured by the "boil" are always high but are sometimes almost explosive.

It may be observed, however, that there exist two new sources of FeO for the metal, which are relatively of little importance during the later stages of the heat; namely, oxidation of Fe by CO_2 bubbling through it and by the direct action of the furnace gases when the metal surface is exposed by the violent boiling In the subsequent portions of this article, these sources will not be considered, thus imposing on the treatment a limitation to the working and finishing periods.

THE DIFFUSION PROCESS

According to the mechanism which has been adopted for the preceding discussion, the rate of carbon elimination from the metal bath is determined by the concentrations of carbon and FeO and the temperature With the temperature constant and the carbon content continuously decreasing, the only remaining controllable factor is the FeO concentration in the metal, and this only through the control of the diffusion process. Although Herty[24] has recently discussed this process in some detail, its importance justifies further treatment.

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[24] C H Herty, Jr Reference of footnote 19, 284

The subject of diffusion may be approached either from a purely theoretical point of view or an empirical one but in either case the starting point is Fick's first law [25]   The law states that the amount of substance dn which diffuses across an interface in the time dt is given

$$\left(\frac{dn}{dt}\right)_s = -DA\frac{dc}{dx} \qquad [16]$$

in which D is the diffusion coefficient, A the area of the interface, $\frac{dc}{dx}$ is the concentration gradient of the diffusing substance, the subscript s refers to the slag so that $\left(\frac{dn}{dt}\right)_s$ is the amount of FeO leaving the slag layer in unit time   The distance dx, for the time being, may be called the "thickness of the diffusion layer," the concentrations of the diffusing substance on the opposite sides of the layer differing by dc The FeO which leaves the slag enters the metal, so that

$$\left(\frac{dn}{dt}\right)_M = -\left(\frac{dn}{dt}\right)_s$$

This, when combined with the obvious relations between amount and concentration

$$\frac{1}{v_s}\left(\frac{dn}{dt}\right)_s = \left(\frac{d[\text{FeO}]_s}{dt}\right)_{\text{diff}} \text{ and } \frac{1}{v_M}\left(\frac{dn}{dt}\right)_M = \left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{diff}}$$

yields

$$\left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{diff}} = -\frac{v_s}{v_M}\left(\frac{d[\text{FeO}]_s}{dt}\right)_{\text{diff}} = \frac{DA}{v_M}\frac{dc}{dx} \qquad [17]$$

The first complication that arises in the application of this equation lies in the determination of the concentration gradient to be used   If we consider the most general case, there must be two concentration gradients involved, one on each side of the interface.   Such a condition is represented in Fig 2 by ABC and $C'DE$ According to Lewis and Whitman,[26] the points where C and C' should be on the interface line depend upon the relative solubility of the diffusing substance in the two phases; i e , the curve ABC might meet the interface line somewhere near

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[25] Piérard (*Loc cit*) has discussed the phenomenon in terms of Fick's second law $\left(\frac{dc}{dt}\right)_x = D\left(\frac{d^2c}{dx^2}\right)_t$ by means of which it is possible to take into account the change in concentration with time in the diffusion layer   This is particularly important where stirring action is absent or small, but with rapid stirring the solution degenerates to equation 16   For this reason the reader is referred to Piérard's article for the somewhat more general case

[26] W K Lewis and W G. Whitman   Principles of Gas Absorption   *Ind & Eng Chem* (1924) **16**, 1215

H while $C'DE$ might meet it near L Herty[27] has already considered this point and placed $C'DE$ much lower than shown in Fig 2   This would localize most of the resistance to the passage of FeO within the slag layer, which is probably correct   Such a condition is approximately indicated by $ABGHE$ Since the actual shape of the concentration-distance curve is not known, it is usually assumed to be linear; e g , BFD and BKH In the absence of sufficient information to make the correct choice among these possibilities, the simplest treatment is to consider that the diffusion determining concentration is linear and lies entirely on the slag side of the interface, as represented by $ABKHE$ This assumption has been used by Feild and by Herty   It is to be observed that a linear concentration gradient means that $\left(\dfrac{dc}{dx}\right)$ = constant, therefore the rate of diffusion is constant according to equation 17   It must be noted, however, that
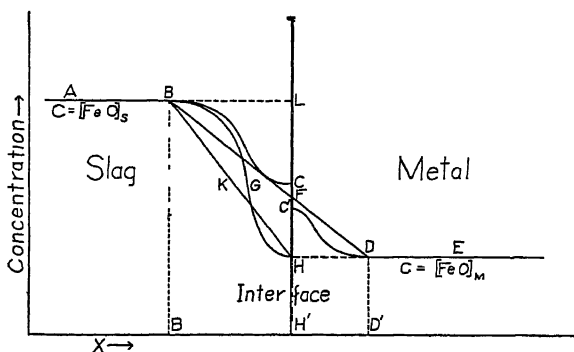
FIG 2 —CURVES OF CONCENTRATION GRADIENT.

neither of Fick's laws takes into account irregular mechanical disturbances such as stirring, which affect the "thickness of the diffusion layer" without disturbing the limiting values of the concentrations   Finally, it is to be recalled that the concentration gradient determining the rate of diffusion is not the difference between the absolute concentrations of FeO in the two phases but the distance from the distribution equilibrium, hence dc is given by $\left([\text{FeO}]_s - \dfrac{[\text{FeO}]_M}{r}\right)$ and not $([\text{FeO}]_s - [\text{FeO}]_M)$
As the working equation we have

$$\left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{diff}} = \frac{DA}{v_M \Delta x}\left([\text{FeO}]_s - \frac{[\text{FeO}]_M}{r}\right) \qquad [18]$$

in which Δx represents the finite thickness of the diffusion layer corresponding to the finite concentration difference   The quantity H in equation 6 is therefore

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[27] C H Herty, Jr   Reference of footnote 24

$$H = \frac{DA}{\Delta z} \qquad [19]$$

The difference between the purely theoretical and empirical methods of treating the problem begins at this point and essentially this difference lies in the way the ratio $\dfrac{D}{\Delta x}$ is handled

From the theoretical viewpoint the diffusion process consists in molecules with a certain effective surface area moving through a viscous medium   As a first approximation, Stokes' law may be assumed to govern such motion and we may therefore write[28]

$$D = b\frac{T}{\eta} \qquad [20]$$

in which b is a numerical coefficient depending theoretically upon the radius of the molecules, η is the viscosity coefficient, T is the temperature. Actually, in certain systems which have been carefully investigated, the temperature coefficient of the diffusion constant seems to depend in part on the value of D itself,[29] so that ultimately it may be necessary to consider b also as a function of temperature   Equation 18 thus becomes

$$\left(\frac{d[FeO]_M}{dt}\right)_{\text{diff}} = \frac{b}{v_M}\frac{AT}{\eta\Delta x}\left([FeO]_s - \frac{[FeO]_M}{r}\right) \qquad [21]$$

Without a knowledge of the value of Δx, however, this equation is of little service, and, as far as the present writer is aware, neither the kinetic theory nor the hydrodynamic has given a quantitative expression for this quantity independent of the diffusion equation itself (equation 17) The general trend of experimental data available indicates (1) that Δx decreases as the rate of stirring increases and (2) that the smaller the value of Δx the more difficult it becomes to decrease it further   In addition, Lewis and Whitman (*op cit*) state that "the ratio of viscosity to density of the film fluid is probably a controlling factor in determining film thickness."

The correctness of the first two statements is aptly illustrated not only by the work of Lewis and Whitman, Haslam, Hershey and Keen, and others[30] on the rate of solution of gases by liquids and the reverse process, but also by the experiments of Edgar, Van Name, Noyes and Whitney, Nernst, and Brunner[31] on the rate of dissolving salts in water, oxides in

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[28] Taylor *Op cit* , 941

[29] Oholm   *Ztsch phys Chem* (1904) **50**, 309, (1910) **70**, 378.   Medd Nobel Inst (1912) **2.**

Taylor. *Op cit* , 938.

[30] For reference to these and other workers on diffusion see Herty, ref of foot-note 24.

[31] Summarized by Taylor: *Op cit* , 943   For additional data and references, see International Critical Tables, **5**, 55

acids, metals, both solid and liquid, in oxidizing solutions and acids The rates of the heterogeneous reactions have been shown to be dependent on the rate of stirring in each case, the arbitrary measure of stirring rate being raised to a power somewhere between zero and unity   There seems to be no general way of defining "rates of stirring" which permits comparison between results of different types of stirring and the data of different investigators

In working and finishing periods of the open-hearth process, where the diffusion process is most important, the principal factor in keeping the bath stirred is the bubbling of CO through the bath, and as a first approximation the rate of stirring might be defined as proportional to the rate of CO evolution, and thus to the rate of carbon oxidation   As the reaction proceeds this rate, and therefore the rate of stirring, decreases so that Δx would probably increase considerably as the bath approaches the "flat" state   Secondary factors which lead to stirring action are the movement of nonmetallic particles from the bottom through the metal (this would affect only the metal layer) and convection currents   Unfortunately for the open-hearth operator, the density differences produced by temperature gradients are in the wrong direction, since the heating is from the top   Density differences in the slag layer due to differences in composition, and of sufficient magnitude to produce any considerable stirring by convection, seem unlikely, and in any case are probably more than compensated by the temperature effects   Stirring action in the slag due to friction of the rapidly moving gases at the slag-gas interface has already been mentioned by Feild [32]

The empirical method of studying the diffusion process is exemplified by the work of Lewis and Whitman and of Haslam, Hershey and Keen already mentioned   By combining $\frac{D}{\Delta x}$ in a single constant called either the "film coefficient" or the "over-all coefficient," depending on whether the effect of the film on only one side of the interface or of both films in series was being considered, equations of the form

$$\frac{dn}{dt} = AK(C - C') \qquad [22]$$

were obtained in which A is the area and K the coefficient   They studied the effect of various rates of stirring (gas velocities) at constant temperature and the effect of various temperatures at constant stirring rates. Their results could be expressed in the form

$$K = aS^pT^q$$

where a is a constant and S a measure of stirring rate—in their work, gas velocity   Since change of temperature affects both the viscosity and the

[32] A L Feild First reference of footnote 1, 117.

density of the film liquid, it was possible to examine the statement by Lewis and Whitman quoted above as to the effect of the ratio of these two quantities   This led directly to the expression

$$K = a'S^p\left(\frac{\delta}{\eta}\right)^l$$

for which their results indicated that the exponents were $p = \frac{4}{5}$ and $l = \frac{2}{3}$, δ is the density, a' an empirical constant   Equation 22 may therefore be written in the form

$$\frac{dn}{dt} = Aa'S^{\frac{4}{5}}\left(\frac{\delta}{\eta}\right)^{\frac{2}{3}}(C - C') \qquad [23]$$

The corresponding equation applying to the open hearth becomes

$$\left(\frac{d[FeO]_M}{dt}\right)_{\text{diff}} = \frac{Aa'}{v_M}S^p\left(\frac{\delta}{\eta}\right)^l\left([FeO]_s - \frac{[FeO]_M}{r}\right) \qquad [24]$$

If we introduce Stokes' law into Fick's law as applied to the gas absorption case, we obtain

$$\frac{dn}{dt} = \frac{b}{a'\eta}\frac{T}{\Delta x}(C - C')$$

and combining this with equation 23, the expression for Δx is

$$\Delta x = \frac{b}{a'}\frac{T}{\eta^{\frac{1}{3}}\delta^{\frac{2}{3}}S^{\frac{4}{5}}}$$

There is an evident discrepancy between this equation and the statement of Lewis and Whitman that the "ratio of viscosity to density of the film fluid is probably a controlling factor in determining film thickness " Possible explanations of this discrepancy which suggest themselves are (1) Lewis and Whitman may be incorrect, although qualitative arguments for an increase in film thickness as the viscosity increases seem to be more satisfactory than for a decrease in the thickness, (2) the quantitative inadequacy of the measure of stirring, (3) the actual form of the concentration gradient; (4) the obvious lack of exactness of Stokes' law as applied to this sort of system

The second of these involves a broad and general problem, the nature of which may be indicated by the consideration that for a given number of revolutions per minute of a propeller or a given linear gas velocity the stirring effect in a fluid of low viscosity must be greater than if the viscosity is high, i e , Δx is decreased more, and this is independent of the direct influence of viscosity on Δx Thus constant rate of stirring as usually defined has little meaning as far as actual effectiveness of stirring is concerned when comparisons are made between liquids of different viscosities.

The third explanation refers to the simplifying assumption discussed earlier and illustrated in Fig 2. Although it is possible in straightfor-

waid determinations of diffusion constants to fix the experimental conditions so that the concentration gradient is essentially linear, the chance that such a simple situation would exist in absorption measurements, and in particular in the open hearth, appears remote If, as seems more likely, the concentrations on the two sides of the "layer" approach their limiting values asymptotically, we would be forced to integrate the general equation $\frac{dc}{dx} = \psi(x)$ between arbitrary limits corresponding to arbitrary fractions of the limiting concentrations, in order to obtain a finite value of Δx In such circumstances it is impossible to predict what the quantitative effects of stirring, viscosity and temperature changes are likely to be It seems certain that the temperature coefficient of D such as was determined by Oholm must be entirely different from the temperature coefficient of a "film" or "over-all coefficient," since the latter includes the factor Δx, which D does not It is to be emphasized, however, that in equation 22 several of the variables, including Δx have been combined and are taken into account in the empirical evaluation of the constants If, for the purpose of the open-hearth problem, we wish to indicate that, due to the varying physical conditions in the bath, H cannot possibly be considered as constant even at a given temperature, we may write

$$H = H_o + \int_{t_1}^{t_2} \left(\frac{dH}{dt}\right)_{\substack{\text{phys} \\ \text{cond}}} dt \qquad [25]$$

in which H_o is the initial value The subscript "physical conditions" indicates that H is dependent upon such factors, temperature still being considered as constant

The various chemical factors affecting the diffusion process must be taken into account by suitable modifications of equation 6 The effect on the FeO content of the slag by ore addition as a function of time cannot be stated in any satisfactory way and must be treated empirically Effects of chemical composition are due to direct changes in the value of $[FeO]_s$ caused principally by diffusion but partly by the reduction of Fe_2O_3 at the slag-metal interface, and by the variation of the distribution coefficient r. The latter is particularly sensitive to variation of the ratio of total bases to total acids in the slag If we are to take these additional factors into consideration, and represent the initial content of FeO in the slag by $[FeO]_{so}$, equation 6 becomes

$$\left(\frac{d[FeO]_M}{dt}\right)_{\text{diff}} = \left[H_o + \int_{1}^{t_2}\left(\frac{dH}{dt}\right)_{\substack{\text{phys} \\ \text{cond}}} dt\right]\left[[FeO]_{so} + \int_{t_1}^{t_2}\left(\frac{d[FeO]_s}{dt}\right)_{\text{diff}} dt + \right.$$

$$\int_{t_1}^{t_2}\left(\frac{d[\text{FeO}]_\delta}{dt}\right)_{\text{Fe}_2\text{O}_3} dt + ([\text{FeO}]_\delta)_{\text{ore}} - \cdots \frac{[\text{FeO}]_{Mo} + \int_{t_1}^{t_2}\left(\dfrac{d[\text{FeO}]_M}{dt}\right)_{\text{total}} dt}{\iota_0 + \int_{t_1}^{t_2}\left(\dfrac{d\iota}{dt}\right)_{\substack{\text{chem} \\ \text{comp}}} dt} \quad [26]$$

Sufficient has been said about the nature of the diffusion process to indicate that some of the fundamental quantities, particularly Δx, have not yet been studied sufficiently to establish their variation with the conditions of the experiment and the properties of the system   Furthermore, and this has been the chief purpose in giving such a detailed discussion, it is evident that in assuming that the stirring is sufficient to avoid stratification one does not eliminate many of the more serious difficulties, and that the application of constants determined empirically for totally different systems and conditions may easily lead to conclusions involving gross errors

The complex nature of the open-hearth process and the very considerable experimental difficulties involved will probably preclude the possibility of direct experimental study of the individual variables in the diffusion process   Progress, therefore, would seem to depend upon empirical studies guided by an equation such as 24 or 26   In view of the fact that physical factors, which are difficult and perhaps impossible to measure and control, play such an important role in determining the diffusion rate, it cannot be too strongly emphasized that the application of results obtained under one set of conditions to a different set must be made with a clear understanding of the implications involved.

SUMMARY

An attempt has been made to analyze the complex set of reactions and processes comprised in the open-hearth steel process   The major premise in this analysis was that the mechanism of the carbon oxidation—i e., the rate-determining reaction—is $\text{FeO} + \text{C} \rightleftarrows \text{Fe} + \text{CO}$ and that this reaction takes place in the molten metal.   On this basis we have concentrated upon the reactions and processes that supply or remove FeO from the metal bath.   Again it must be emphasized that if FeO is not involved in the rate-determining reaction all that has been said may be discarded immediately and another approach must be made to the problem on the basis of a different mechanism

Furthermore, it has been implied throughout that constants for individual reaction velocities and physical processes will have the same values when all of them are proceeding simultaneously as when determined independently in more restricted systems.   This implication requires discussion

In the case of the velocity constants of the chemical reactions it has been assumed that each reaction proceeds independently of the

others except in so far as the concurrent reactions and processes influence the concentrations of carbon and FeO   For example, if the carbon oxidation is catalyzed by other elements the situation at once becomes tremendously more complex   Not only must the catalytic effect, which may be either to increase or to decrease the rate, be determined but the variation of catalyst concentration during the reaction becomes an indispensable part of the required information   The values of k_F for the individual reactions thus become complex functions of time

As for the physical processes, the greatest stumbling block to the quantitative applications of theoretical considerations lies in the unknown variation of the "constant" H in the diffusion equations   Especially during the working period, variations of this quantity may exercise greater influence over the rate of carbon elimination than any other single quantity considered   In view of the fact that it is dependent upon physical or mechanical factors such as rate of stirring and viscosity, as well as upon the chemical composition, the application of laboratory values to plant conditions is hazardous if not foolish

As each new reaction that affected the FeO content of the metal was discussed, it was pointed out that according to the present method of approach we should add another term to equation 5   It is now appropriate to set down equation 5 modified in this way but also including the last equation for the diffusion rate to illustrate how complex and unwieldy the result becomes   The following equation, however, is by no means the most complicated form that an equation which attempts to be a general representation of the open-hearth process might assume, even when limited to working and finishing periods:

$$\left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{total}} = \frac{d[\text{C}]}{dt} + \left(H_o + (\Delta H)_{\substack{\text{phys} \\ \text{cond}}}\right)\left[[\text{FeO}]_{so} + (\Delta[\text{FeO}]_s)_{\text{diff}}\right.$$

$$+ (\Delta[\text{FeO}_s])_{\text{Fe}_2\text{O}_3} + ([\text{FeO}]_s)_{\text{ore}} - \left.\frac{[\text{FeO}]_{Mo} + (\Delta[\text{FeO}]_M)_{\text{total}}}{r + (\Delta r)_{\text{comp}}^{\text{chem}}}\right] +$$

$$\left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{Mn}} + \left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{Si}} + \left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{P}} + \left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{Fe}_2\text{O}_3} \quad [27]$$

The subscript o refers to initial conditions, the others in order from left to right refer to physical conditions, diffusion, Fe_2O_3 reduction, ore addition, chemical composition, manganese, silicon and phosphorus oxidation, and Fe_2O_3 reduction   Each of the quantities of the form ΔH, $\Delta[\text{FeO}]_s$, etc. are abbreviations for terms of the form $\int_{t_1}^{t_2}\left(\frac{dH}{dt}\right)dt$ with the corresponding subscript for the differential coefficient.

This equation, despite the multiplicity of terms, is a complete differential for the variation of $[\text{FeO}]_M$ with time only for the "closed" system as described   It is true that this "closed" system is much more

complex than that described by equation 3, but if there are still other processes involved in the open hearth which affect the value of $[FeO]_M$ and which have not been accounted for by terms in equation 27, this equation is likewise an incomplete differential   Its accuracy depends upon the accuracy of our description of the process as a whole

This equation has been put in the form for solving for the variation of $[FeO]_M$ with time rather transposing $\dfrac{d[C]}{dt}$ to the left of the equality sign to emphasize the fact that on the basis of our major premise the open-hearth process is a series of processes for the purpose of changing the FeO content of the metal   In this series the oxidation of carbon is only one incident, even though it may be the major problem for the steel manufacturer   When it is realized (1) that each one of the terms on the right is itself a complex quantity, (2) that nothing has been said about carbon elimination by the reaction $MnO + C \rightleftarrows Mn + CO$ and similar reactions, (3) that there is no term covering the oxidation of FeO in the slag by furnace gases and (4) that the equation holds only for constant temperatures, it is seen that the derivation and application of a general equation, which must of necessity include the temperature factor, is indeed almost hopeless.

Nevertheless there are certain values to be gained from such an analysis, which may be enumerated in part as follows·

1   From the kinetic standpoint a knowledge of the FeO content of the metal during the various stages of the heat is even more important than carbon content

2   The application of diffusion constants, whether determined in the laboratory or from open-hearth data, is more than likely to lead to false results, because of the impossibility of measuring and controlling certain physical and mechanical conditions which determine the actual value and which vary considerably from heat to heat and furnace to furnace.   As far as the diffusion process is concerned, the phrase "under comparative conditions" means little or nothing

3   As long as open-hearth practice continues in the use of highly oxidizing finishing slags "overoxidation" is unavoidable.   The rate of diffusion of FeO from slag to metal can be reduced by decreasing the FeO content of the slag or by lowering the distribution constant $r = \dfrac{[FeO]_M}{[FeO]_s}$.   The latter may be attained by increasing the SiO_2 content; e g , the acid open-hearth process.

4.   The theoretical considerations leading finally to equation 27 also have a value in outlining research   Although it is probably impossible to secure a complete equation for the problem, and impracticable to use such an equation even if it and all of its contents could be found, considerable progress can still be made by an intelligent grouping of several of the

terms and variables   In some plants where steel or a comparatively restricted range of composition and properties are made almost exclusively or for a single furnace which is used for only one kind of steel, it is not impossible that a simple empirical equation containing temperature as one of the variables can be obtained from a careful study of the operations over a period of time   Such an equation, of course, would possess little, if any, theoretical significance   In melting certain special steels, certain terms in the equation become more important than others   For a high-manganese steel scrap, the term $\left(\dfrac{d[\text{FeO}]_N}{dt}\right)_{Mn}$ would be of the same importance as the rate of carbon elimination

5 Finally, the preceding analysis of the problem indicates that for the purpose of making progress it is a matter of necessity that studies of individual reactions and processes, whether made in the laboratory or in a furnace of commercial size, must be appreciated in their relation to the process as a whole as expressed by equation 27 or some other more suitable but at least equally general equation   With this end in mind, all data which are to be interpreted from the kinetic viewpoint must be accompanied by an accurate description of the conditions under which they were obtained   As has been mentioned, it is the lack of knowledge and, in some cases, the lack of an adequate measure of certain physical and mechanical conditions within the system under investigation, that is the greatest obstacle to the proper understanding and correlation of data and to the application of theory to the open-hearth process.

DISCUSSION

(John Johnston presiding)

L F REINARTZ, Middletown, Ohio (written discussion) —As a practical open-hearth operator, I was rather embarrassed to find that I had agreed to discuss such a highly technical and mathematical presentation of the kinetics of the open-hearth process   Therefore I asked Mr J E Lucas, of the Research Laboratories of the American Rolling Mill Co , to give me his interpretation of this paper   I quote from his reply.

"The accompanying article on open-hearth processes seems to me to represent an entirely new method of attack of the problem of elimination of metalloids in the open-hearth furnace.   The author has recognized that the problem of carbon elimi-

nation cannot be separated from the other reactions which are proceeding simultaneously, and attempts to include all in a mathematical expression   The paper makes apparent the need for basic research in the thermodynamic problems of the open hearth, namely, the diffusion and reaction rates which obtain for the conditions present and also the discovery of the correct mechanisms whereby these reactions take place.   It is only by having correct quantitative knowledge of these data that we may learn how better to control the reactions   As the author points out, the controlling factor in carbon elimination, as well as other metalloids, depends upon which rate governs, that is, whether the reaction rate is slower or faster than the rate of diffusion of FeO from slag to metal and whether the reaction takes place entirely in the metal layer or at the slag-metal interface

"Heretofore, the work of Herty and Gaines has seemed to indicate an equilibrium during the larger portion of the heat by the FeO and carbon in the metal layer Jette, however, points out that this assumption is based on data of which the values may be controlled by these conditions rather than being due to a chemical equilibrium One point of immediate practical application is the possible explanation of the slowing up of carbon elimination toward the end of the heat   This slowing up has been explained on a basis that the reaction tended to reverse itself because of the development of a high pressure of CO in the metal   This high pressure, of course, represents a supersaturated condition and, owing to the dead condition of the bath at this time, is entirely possible   The practice of using poles in the heat to remove the last traces of carbon may be justified on this basis, that is, that the stirring action due to the boiling produced by these poles tends to break up the supersaturated CO solution, thus allowing the elimination of carbon to complete itself rapidly, since sufficient time has previously been allowed for complete equilibrium distribution of FeO between slag and metal to take place"

Personally I am glad our physical chemists are taking an active interest in the interpretation of the complex reactions in an open-hearth bath   I do not believe that at the present time it is possible to write a comprehensive equation that will give a true picture of the open-hearth process   The system certainly is not a closed one and many factors have a direct and indirect bearing on the iron oxide-carbon rate of reaction and diffusion   That these rates have a profound bearing on the practical operation of an open-hearth furnace is self-evident

COMPLEX FACTORS IN WORKING A HEAT

The open-hearth operator has many complex factors to keep constantly in mind during the working of a heat, the chief of which probably are slag constitution and reactions   The practical operator knows that increase in MgO and SiO₂ in the slag will thicken the slag and decrease the reaction rate   He knows that fluorspar, chloride of lime, soda ash, manganese oxide, by making the slag more fluid, will increase the speed of the reaction   A thin slag will absorb iron oxide more rapidly than a thick one   A slag of small volume will allow reactions to proceed more rapidly than a slag of large volume   The relation of area of bath to total volume of metal and slag has a marked influence on the reaction and the diffusion rate of the bath of metal

I cannot believe that the diffusion rate, as such, has a very marked bearing on the speed of reactions in an open-hearth furnace despite the claims made by some metallurgists that this effect is very important   Reactions under a quiet slag proceed very slowly if no mechanical or other stirring action is introduced in the bath   In addition, the design of a furnace and the kind of fuel has a distinct bearing on the reaction rate   The age of the furnace often will determine the rate of the heat input.

Natural gas, with its sharp flame, does not allow reactions to proceed as rapidly after the metal is all melted as a producer gas flame, with its highly luminous radiating flame

The kind of charge must also be considered Is the charge composed of coke and scrap, pig iron and scrap, hot metal and scrap? What are the proportions of these metals and what the analysis? Silicon in the charge, particularly, has an important bearing on the reaction rate of the heat after it is melted An extremely low silicon input will cause a heat to melt "dead " The temperature will not be sufficient to allow the iron oxide carbon reaction to proceed at a normal rate In these days when every one is driving for increased output per hour per unit, it is important to the open-hearth operator to know how to regulate and speed up the rate of reaction in an open-hearth furnace without serious detriment to quality He knows that the addition of iron ore will speed up the reaction rate He may have his choice of lump or fine ore and invariably will choose the lump ore in order to react directly with the carbon in the bath rather than use the slower process of increasing the iron oxide in the slag by the use of fine ore and then depend on the slag-metal interface reaction

The operator wants to know how soon he dare "ore" the bath, how much he may add at a given time, how long each reaction should take and how close to the time of tapping he dare add "ore " These are practical questions he wants answered

The theory that high temperature will reduce carbon more rapidly than a lower temperature does not agree with practical observations A bath must not be worked too hot or the reaction rate will slow down

SOLUBILITY OF CO IN BATH

I am anxious to have more light thrown on the question of CO solution in the metal bath It has always seemed to me that in steels very low in carbon, where the concentration of iron oxide is high and carbon is low, there must be a very considerable percentage by volume of CO gas in a supersaturated solution When such low-carbon steel or iron is poured into a mold, it "gasses" much longer than a heat containing 0 10 per cent carbon made on a rimming basis It would appear to the observer that considerable gas was coming out of solution rather than that the gas was entirely the product of a carbon-iron oxide reaction in the mold

R S DEAN, Washington, D C (written discussion*) —The author is right in emphasizing the fact that if the essential and rate determining reaction in the open hearth is not the homogeneous reaction

$$FeO + C \rightarrow CO + Fe \qquad [1]$$

all that he has said may be discarded immediately, and also what others have said in like vein It seems to me that an undue amount of work is being done on this questionable assumption In the first place, the assumption that a homogeneous reaction like [1] at 1600° C should proceed more slowly than diffusion, as required by the experiments quoted on page 95, seems strained The treatment of the above reaction as a homogeneous reaction also infers a finite solubility of CO in molten iron, an unproved and not too probable a theory The further assumption is made that the reactions

$$CO_2 + C \rightleftarrows 2CO \qquad [2]$$

and

$$CO + FeO \rightleftarrows Fe + CO_2 \qquad [3]$$

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proceed at a negligibly slow rate compared to [1]   Otherwise we must treat the system as univariant, and if we fix the pressure at one atmosphere, it must proceed at one temperature until one of the components is eliminated

I am not at all sure that the attempt of the physical chemist to carry over conceptions developed for aqueous solution to metallic melts is well advised   These slag-metal reactions so common in metallurgy may perhaps be more profitably treated as surface reactions, in which the important factors become the degree of dispersion of the slag melt in the metal, or vice versa, and the nature of the protective film on the disperse particles   This conception does not lend itself so well to mental gymnastics, but I believe it can be shown to be more useful in coordinating the facts, as for example

The consequences of a negligible solubility of CO in steel lead to a number of conclusions seemingly in accord with the facts   Reaction 1 cannot take place spontaneously throughout a bath of steel with the production of a separate phase of CO, since this must give a haphazard mixture of CO + Fe atoms which would constitute miscibility, accordingly, the reaction will take place only at the phase boundary of CO and will therefore be "unimolecular" and of measurable rate, as Scandelin observed

A similar explanation has been put forward by Langmuir to account for the rate of decomposition of $CaCO_3$ on heating

As a further consequence of CO insolubility, particles of FeO in the bath will acquire a film of CO which might well result in a considerable lifting force SiO_2, on the other hand, will acquire no such film   Perhaps the difference in rate of rise of SiO_2 and FeO particles in a bath is just accounted for by some such flotation process

I shall not pursue this subject further here but hope at a later time to show in detail the physical if not the mathematical advantages of this conception of the mechanism of metallurgical reactions

DEVELOPMENT OF EQUATION 7

H STYRI, Philadelphia, Pa (written discussion) —The step by step method used by the author is a cautious method but does not insure against mistakes   The development of equation 7 by setting

$\left(\dfrac{d[\text{FeO}]_M}{dt}\right)_{\text{total}}$ in equation 5 $= \dfrac{d[\text{FeO}]_M}{dt}$ in equation 2 is faulty because the latter

represents $\left(\dfrac{d[\text{FeO}]_M}{dt}\right)_{\text{react}}$, which may be understood from the following reasoning

If [C] and [O] are the concentrations of C and O respectively in a closed system of steel only, the rate of change for both C and O is expressed by.

$$-\frac{d[\text{C}]}{dt} = -\frac{d[\text{O}]_M}{dt} = k_F[\text{C}] \times [\text{O}]_M - k_B[\text{CO}]$$

since both elements react with the same number of atoms

In another system—for instance, with an oxidizing slag on top of the steel, in which the concentrations of C and O are identically the same as in the first closed system—the initial rate of change i of [C] is also expressed by the same

$$k_F[\text{C}] \times [\text{O}]_M - k_B[\text{CO}]$$

and must, of course, give the same

$$-\frac{d[\text{C}]}{dt} \text{ and } -\frac{d[\text{O}]_M}{dt} \text{ react}$$

as in the first case, however much $[\text{O}]_M$ stands for the total oxygen dissolved in the metal at that instant

Solving equation 1 for FeO_M and differentiating we get:

$$-\frac{d[FeO]_M}{dt} = -\frac{1}{k_F[C]^2}\left(\frac{d[C]}{dt}\right)^2 + \frac{m[CO]}{[C]^2}\frac{d[C]}{dt} + \frac{1}{k_F[C]}\frac{d^2[C]}{dt^2} - \frac{m}{[C]}\frac{d[CO]}{dt}$$

where the members to the right are the four last members in equation 7 Now since equation 1 gives the rate of reaction in the metal both in the closed and open system with identically the same concentrations of C and O at the same instant, $\frac{d(FeO)_M}{dt}$ can only represent the rate of reaction of the O in the metal of both systems. The four members therefore are equal dC/dt and make equation 7 collapse

No effect of diffusion from the slag is shown in this formula

If we want to find the total change of FeO in the metal the diffusion must be taken in account according to equation 5

DEVELOPMENT OF EQUATIONS 8 TO 11

Jette's second and third method of approach seem mathematically correct but it is difficult to see any advantage in developing equation 8 One may wonder if the development of equations 8 and 11 have been made in order to facilitate integration or in order to see whether 7 and 11 are identical and could be transformed into 8 They do not serve any purpose in the subsequent discussion of "cases " It is evident from that discussion that equation 5, or none at all, would be better for that purpose

In case I, Jette has referred to the unimolecular reaction type discussed by the writer in a previous paper[33] but there is the difference that in arriving at this equation the writer considered what he later called an "open system" in which we have a continuous oxidation of the melt from the atmosphere or by ore additions The metal, however, was not saturated with FeO in the sense assumed by Jette, as being in equilibrium with slag It was then stated that the reaction was of the unimolecular type because, in studying the carbon drop in the open-hearth furnace where temperature and slag condition were kept constant the log C was found to be practically a straight line against time, which should be the case if the concentration of one of the reacting substances (here O) were constant In further discussing the reaction, it was stated (page 217) that in the beginning the oxygen would be used up faster than later at lower carbon concentration Consequently, the O concentration would increase gradually but any effect of this on the rate was not evident. The apparent constancy of O depended, of course, on the diffusion of O from atmosphere and slag De Loisy's development, which the writer has previously discussed,[34] was considered erroneous because it led to a rate of carbon elimination inversely proportional to the square of the depth of the metal

The author bases his case II on the supposition that FeO is much higher than the quantity that should be in equilibrium with carbon in the steel Such condition would not be usual in cold melt open-hearth practice and can only be thought possible for very short periods when ore or oxidized molten iron is added to the bath or when molten pig iron is added to a highly oxidized iron Due to the limited solubility of oxygen, the momentary excess in such a mixture will be used up rapidly and would be of no consequence for the continued elimination of carbon

In case III the author assumes a reaction rate which is much higher than the diffusion rate This statement in the headline is somewhat misleading in view of what has just been said about the limited solubility of oxygen. The reaction rate,

[33] H Styri: *Jnl.* Iron and Steel Inst (1923)
[34] Iron and Steel Technology in 1928, A. I M. E. (1928) 137.

of course, being proportionate to the product of carbon and oxygen in the solution, would decrease rapidly with rapid decrease in either of these factors   The author evidently means by high reaction rate that the factor k_F is large

If the author's case IV should be possible, a sample scooped out and poured in a test mold should boil violently, much more than a sample taken from the bath during the usual boil

DIFFUSION OF OXYGEN

The author has been very successful in his mathematical demonstration that a high value of the so-called practical equilibrium constant may be due to an excess diffusion of oxygen into the bath   If equation 15a is written in the form $-\dfrac{d[C]}{dt} =$

$$\frac{\left[\dfrac{d\mathrm{FeO}_M}{dt}\right]_{\mathrm{diff}}}{1 + \dfrac{[\mathrm{FeO}]_{0\,M}}{[C]_0}}$$ it is easy to see how dominant a factor the diffusion is in the elimination

of carbon, particularly at higher values of carbon   A determination of k_F from $-\dfrac{d[C]}{dt} = k_F[C] \times [\mathrm{FeO}]_M$ when $[C] \times [\mathrm{FeO}]_M$ appears to be constant does not give the real velocity constant k_F but only, as the author states, an apparent constant, because the analyzed [FeO] also contains the O bound inactively to other elements Si, Mn and Al suspended in the melt

It may be of interest in this connection to refer to a recent paper by Herty,[35] where it appears from the graphs of three heats given that the carbon drop on a 0 50 C steel averaged about 0 0033 per cent C per minute for a product FeO × C about 0 04, while for 0 30 C steel there was a drop of 0 003 per cent C per minute for a product equal to 0 02 and for a 0 12 C steel a drop in carbon of 0 0016 per cent C per minute for a product 0 023   In other words, the drop in carbon was evidently not proportionate to the product FeO × C   If we subtract from these values Herty's constant 0 01 (m) the difference will be still greater   The values are taken from the graph and are, of course, not accurate

The author's reference to Sandelin's paper is very timely, as it may help to clear up some cause for the discrepancies in determining the constant m Sandelin shows that Mn is oxidized at a rate indicating an apparently constant concentration of oxygen in the steel at a time when carbon is not noticeably affected   This should indicate also that the concentration of oxygen should be higher than corresponding to the Mn × O equilibrium but smaller than the C × O equilibrium   This state of reaction may be explained equally well by a nearly constant rate of diffusion of oxygen into the steel bath   Some of the manganese oxide formed will not rise to the surface but will be present as slag inclusions and, of course, the oxygen tied up with this manganese would be analyzed as oxygen in the vacuum fusion process and included in the total oxygen while it actually has no effect on the elimination of carbon   The same is true for the other oxides of silicon and aluminum   It is, therefore, essential that in studying the carbon elimination and change in concentration of oxygen the content of other elements in the steel as well as in the slag be given throughout the heat

The author's academic study of the diffusion process cannot be said to have any bearing on the usual open-hearth process, because it covers only a closed system with a fixed quantity of slag, a limitation which is stated by the author   In the regular

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[35] C H Herty, Jr   *Metal Progress* (Feb , 1931).

open-hearth process, the effect of furnace gases and ore additions is much more important   The writer believes that we would learn much more about open-hearth processes by carefully studying and analyzing the process itself guided by such a simple equation as No 5, which states that the sum of oxygen used in elimination of carbon and the other elements plus the oxygen absorbed in the metal is equal to the oxygen diffused into the metal

The author has been very careful in repeatedly pointing out the limitations of his study and it must be granted that he has done a thorough and careful work, but too much mathematics has led him to adopt Feild's mystic equation 7   The author has shown clearly the futility of this kind of mathematical attack on the open-hearth problem, which has led to a veritable jungle even without considering perhaps the most important factor in the open-hearth operation, namely, the furnace atmosphere.

It is evident that our attention should be concentrated more in experimental investigation

Effect of Solubility of CO

A L Feild, Lockport, N Y —This work is a splendid contribution to our knowledge of the open-hearth process   The paper appeals to the student and will point the way to laboratory work   I challenge Mr Dean's remarks that if CO has no solubility the equation is worthless   The question is not a case of solubility but of partial pressure, as solubility does not enter into the equation and the insolubility of CO has already been considered

C. H Herty, Jr , Pittsburgh, Pa —Regarding Mr Dean's discussion, we have assumed that the pressure of CO is constant or builds up at the end of the heat, the solubility of CO is not considered   I congratulate Dr Jette on his study of diffusion, as this is more important than the rate of the oxidation reaction with FeO

Reactions during Finishing and Deoxidizing Stages

E C Bitzer, Youngstown, Ohio (written discussion) —Professor Jette has brought up a vital subject in his paper on the speed of open-hearth reactions, and his efforts on a subject about which so little is known are to be commended   As he stated in his paper, an accurate equation that would include all the factors incident to the removal of any one compound from the metal during the progress of the heat would be too unwieldy and complicated for practical use

However, some possible lines of research investigation have been outlined in the paper, and it seems logical at present to secure data that will make his reasoning apply to the reactions in the bath during the finishing and deoxidizing stages of open-hearth heats   Herty has demonstrated the importance of the speed of reactions as applied to reboiling with various deoxidizers, also, in forming types of inclusions, resulting from deoxidizers, that leave the steel readily

A type of steel which has received very little attention from research workers is rimming or effervescing steel   In this the rate of carbon elimination in the bath has a direct relation to the manner in which the metal acts in the molds, and this in turn affects the quality of the steel rolled from the ingots   It is not necessary to discuss here all of the factors that affect the reaction of the steel in the molds, among which are FeO, manganese, carbon and sulfur contents of the steel, and most important of all, the pouring temperature

Equation 4 of the paper may be made to apply to the iron oxide-carbon reaction in the molds if the proper constants are introduced to allow for the factors mentioned

above   Indeed, it appears that this would be an ideal stage of the process in which to study the speed of the iron oxide-carbon reaction in the absence of a slag   The results obtained would probably not be applicable to conditions in the bath, but many things could be learned that are not now known.   The change in equilibrium due to CO pressure in the steel could be determined more easily here, because it would be possible to have a degree of control over the CO resulting from the rimming reaction   It would also be interesting to compare the equilibrium constant obtained here with that already obtained by other methods, because a properly made heat of rimmed steel is not far from equilibrium so far as carbon and FeO contents are concerned

The matter of the mechanism of the iron oxide-carbon reaction is in question, although all investigators have heretofore assumed it to be $C + FeO \rightleftarrows Fe + CO$. The heat of formation of Fe_3C is very small and it does not seem likely that the rate of formation of this compound would be affected to a great extent by bath temperatures.   If this is true, the formation of Fe_3C is not the rate-governing reaction in carbon elimination, and the mechanism of this reaction could easily be

$$Fe_3C + FeO \rightleftarrows 4Fe + CO.$$
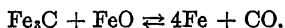
The only proof, if it may be called such, that carbon exists as Fe_3C at carbon contents below about 0 80 per cent lies in the change in appearance of open-hearth fracture tests at about this point.   At higher carbons, during the early stage of the lime boil, the fracture appears gray, which indicates the presence of graphitic carbon   Later, the fracture changes and the metal takes on a silvery luster, which continues for the remainder of the heat   It can be assumed that the transition from a gray to a silvery fracture indicates that all of the carbon has been dissolved and is in the form of Fe_3C

Views Deducible from Thermodynamics

Yap, Chu-Phay, New York, N Y (written discussion) —Professor Jette's paper is very timely and illuminating   Speaking for myself, it has helped to clarify much of the confusion existing at present   It is the clearest and most logical presentation of the theoretical aspects of the problems involved in the open-hearth process   In his careful and systematic analysis of the scope and limitations of the different equations, Professor Jette serves warning upon us to take stock and assay our present knowledge of the physical chemistry of the melt, in order to separate what is theoretically sound from what is theoretically unsound

I should like to supplement Professor Jette's discussions with certain views which are deducible from thermodynamics   He has assumed in his discussions that only equation A represents substantially the chemical reaction in the melt in so far as carbon is concerned, although experimental proof is lacking   I have shown[36] certain evidence which strongly supports the conclusion that the solute in the melt is Fe_3C and not carbon, as has been held for years   The assumption that at 1600° C all the Fe_3C may be completely dissociated can be critically analyzed as follows

What we are interested in is the dissociation equilibrium of Fe_3C in the melt according to the change in the free energy of the following reaction at 1600° C ·

$$3Fe(l) + C(l) = Fe_3C(l); \quad \Delta F_1^\circ \qquad [1]$$

[36] Yap, C -P   A Thermodynamic Study of the Phasial Equilibria in the System Iron-carbon   A I M E *Tech Pub* 381 (1931).   (Abstract on page 141)

Influence of Dissolved Carbide on the Equilibria of the System Iron-carbon A I M E *Tech Pub* 382 (1931)   (Abstract on page 142)

and what I have been working on is the change in the free energy of formation of Fe_3C in the solid state, as shown in the following equation

$$3Fe(s) + C(s) = Fe_3C(s); \quad \Delta F_2° \qquad [2]$$

In order to arrive at equation 1 from equation 2, we have to introduce the following free energy equations

$$3Fe(s) = 3Fe(l); \quad \Delta F_3° \qquad [3]$$

$$C(s) = C(l), \quad \Delta F_4° \qquad [4]$$

$$Fe_3C(s) = Fe_3C(l), \quad \Delta F_5° \qquad [5]$$

By combining these three equations with equation 2, we obtain

$$\Delta F_1° = \Delta F_2° - \Delta F_3° - \Delta F_4° + \Delta F_5° \qquad [6]$$

From the free energy equation 1, we know that at 1600° C

$$\Delta F°_{1873-1} = -RT \ln K_1$$

so that on the assumption that Fe_3C is dissociated only to 90 per cent, ΔF_1 is calculated to be of the order of +10,000 cal , which should also be the value of summation of the terms on the right-hand side of equation 6.

Let us approximate roughly the probable magnitude of the different terms on the right-hand side of equation 6·

$\Delta F_2°$ I have extrapolated my calculations up to 1100° C to 1600° C and obtained a value of somewhere around −8000 cal. Although actually my calculations are made not on the basis of standard state, nevertheless no very great error is involved

$\Delta F_3°$ Since at the melting point of iron (about 1530° C) $\Delta F_3°$ is zero, at 1600° C , it should be (−) in sign and a small value only.

$\Delta F_4°$. Although 1600° C is about halfway from the melting point of carbon, none of the various empirical rules will enable us to calculate the heat of fusion within 500 per cent [37] However, we know that $\Delta F_4°$ will be (+) in sign and a fairly large value

$\Delta F_5°$ As the melting point of Fe_3C is somewhere around 1850° to 1930° C , we know that $\Delta F_5°$ will be rather small and (+) in sign

The sum of $\Delta F_3°$ and $\Delta F_5°$ (as $\Delta F_4°$ in the process of the summation becomes (−) in sign and would, therefore, tend to increase the value of $\Delta F_2°$) must be of the order of 18,000 cal in order to make $\Delta F_1 = +10,000$ cal This is quite improbable because, as noted above, both $\Delta F_3°$ and $\Delta F_5°$ will be rather small values In order that $\Delta F_1°$ may approach a value of +10,000 cal , my value of $\Delta F_1°$ must first be assumed to be absolutely wrong This is possible, though highly improbable While I am not yet free to present before you at this time the basis of my calculations of $\Delta F_2°$ as my studies are not completed, nevertheless, I should like to point out that I am not alone in asserting that $\Delta F_2°$ becomes minus at some temperature around 800° to 900° C , as inferred from the work of Matsubara and Johansson and von Seth Although all the approximations I have made are very rough ones, they enable us to predict the direction of the dissociation equilibrium of my equation 1 As a matter of interest,

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[37] Although we do not know whether or not carbon can actually melt to the liquid state, we are still justified in setting up the free energy equation 4.

I might point out that from equation 6 we learn that as the temperature decreases, Fe_3C should become more and more stable

Of course, I have calculated all changes in free energy on the basis of the standard state (in which the activity is considered unity), but it is not probable that even the most extreme deviation from the standard state conceivable can cause such a difference as to make $\Delta F_1° = +10,000$ cal   The presence of additional constituents in the melt (such as, silicon, sulfur, phosphorus, etc) may affect the value of $\Delta F_1°$ to some extent, and this fact alone may account for the deviation of the Carpenter and Keeling liquidus from the ideal liquidus obtained by Ruer and Goerens using very pure iron-carbon alloys   The former used only what we would call commercial steels, containing an appreciable quantity of other kinds of solute

Coming back to the kinetics of the reactions in the melt, I am strongly inclined to support the fourth possibility presented by Professor Jette, with the reservation that although carbon and Fe_3C are oxidized at the same time, their rates of reaction are, however, not independent of each other, as will be shown below   Reaction A will take place only as fast as the rate of dissociation of Fe_3C according to equation B going backwards   Concurrently, reaction C is also taking place in the melt, so that there is at the same time a tendency for reaction A to go backward, unless CO escapes at once from the system (that is, from the field of reaction)   Hence, we see at once that the rate of carbon elimination from the melt is much more complicated than that shown and discussed by Professor Jette   The assumption originally made by Feild, that all the solute in the melt is carbon, has considerably simplified, of course, the problems involved   I am personally inclined to the view that reaction C is the dominant factor in the reaction rate of carbon elimination and that actually the rate of carbon elimination represents the algebraic summation of the rates expressed by equations A, B and C   If we start with the assumption that Fe_3C already exists in the melt, it is tantamount to saying that forward reaction of B is enormously more rapid than in C, hence the experimental values obtained on the rates of reaction cannot decide for us what the actual mechanism of the carbon elimination is in the melt

I present for the author's consideration these views for two reasons (1) I believe the usefulness of a paper treating the physical chemistry of the melt from a strictly kinetic viewpoint can be considerably enhanced by occasionally introducing thermodynamic treatment, and (2) I hope Professor Jette will prepare another paper on this subject, considering it from other relevant points of view   The auspicious start he has made in this very complicated field bids fair to lead to effective solutions of the fundamental problems involved in the steelmaking processes

PROBLEMS OF DIFFUSION PROCESS

A B Kinzel, New York, N Y (written discussion) —This study by Dr Jette is a searching critique of our present ideas as to the mechanism of the open-hearth reaction   As such, it is most timely and helpful.

It is particularly interesting that Dr Jette arrives at the same general equation for the carbon oxidation in the open hearth as did Feild   This, of course, was inevitable, as the same basic assumptions were made   Dr. Jette's practice of carefully stating and labeling each assumption is gratifying and certainly helps toward clear thinking on this problem   As Dr Jette has covered the probable assumptions, and as the reasoning and physical chemistry resulting from these assumptions are mathematically accurate, no further discussion of these phases is necessary, except to emphasize that additional progress in work of this nature is dependent on quantitative data not as yet available

The attack on the problem of the diffusion process is original and well worth while. Unfortunately, we are not at the stage at which the results of this reasoning may be

applied, except as it emphasizes the possibilities of finally finishing steel under a heavy slag so that higher FeO content may be used with less diffusion of FeO to the bath This suggests the addition of lime or dolomite at the very end of the heat, the latter is preferable, as in this case some of the FeO would be removed from the sphere of action by the magnesia, and the effect of FeO diffusion still further reduced This is only one illustration of how proper understanding of the mechanism may eventually affect open-hearth practice, and we are certainly indebted to Dr Jette for this very clear expostulation of the fundamentals

AUTHOR'S REPLY TO DISCUSSION

E R JETTE (written discussion) —Mr Dean regards the assumption that a homogeneous reaction like A can proceed more slowly at 1600° C than the diffusion process as strained This objection, however, cannot be considered as a fundamental one Although homogeneous reactions usually do proceed faster than diffusion processes, this is by no means universally true Diffusion rates have considerable temperature coefficients of their own, and while for the particular system concerned absence of data makes it impossible to decide in any final manner, it is neither impossible nor improbable for the diffusion rate to supply FeO to the metal bath more rapidly than the reaction uses it

The inclusion of the terms involving CO concentrations arose from the writer's belief that, until proof to the contrary became available, it seemed best to assume that reaction A was a reversible chemical reaction and this naturally implies a finite, although perhaps unmeasurably small, concentration of CO dissolved in molten iron From the kinetic standpoint, however, it is not essential that this reaction be reversible and should it be shown to behave, for example, like the decompositions of hydrogen peroxide, it would only be necessary to drop the terms which take the reverse action into account

When the paper was written, the only directly determined (laboratory) value of the equilibrium constant for reaction A was that of Kinzel and Egan Since the rate of a reversible reaction is proportional to its distance from equilibrium, it may be well to point out that a higher value of the equilibrium constant, such as Vacher and Hamilton found, means that the backward reaction becomes important at an earlier time. The discussion even of such simple situations as those given by cases I, II and III must then either be limited to rather high values of the product $[FeO]_M[C]$ or the equations given must be modified to include the backward reaction.

The reactions numbered 2 and 3 by Mr Dean were omitted from the discussion but not because they had escaped the author's attention In an early draft of the article a section dealing with reactions during the lime boil was included and reaction 2 and the reversal of 3 were considered This section was eliminated for various reasons, as stated on page 101, and the two reactions were not included in the remainder because they seemed of importance chiefly during this period The author, however, has no unshakable convictions on this point

Mr Dean's suggestion of a more physical theory of the open-hearth reactions is not beyond possibility and the writer will be much interested in a detailed account of it

Mr Styri's criticism of equation 7 and its derivation is erroneous While it is correct that equation 1 gives the rate of reaction in both an open and closed system, the same is true of equation 2, and, likewise, of the equation given by Mr Styri, which is obtained from equation 2 merely by substituting the value of $[FeO]_M$ from equation 1

The discrepancy in Mr Styri's reasoning lies in assuming that one can set $\frac{[dC]}{dt} =$ $\left(\frac{d[\text{FeO}\,_M]}{dt}\right)_{\text{react}} = \left(\frac{d[\text{FeO}]_M}{dt}\right)_{\text{total}}$ for both the closed and open systems which he discusses   It is obviously true for the former but not for the latter   One does not put new restrictions on an equation when merely differentiating it with respect to time   While it must be confessed that equation 7 is long, unwieldy and probably of no direct practical usefulness, there is nothing at all mystical about it, as Mr Styri states at the end of his discussion

Mr Styri comments on the choice of the individual cases in applying the ideas on reaction rates and evidently believes that they have little bearing on cases which actually arise   This may be largely true   In choosing these particular situations for discussion, the writer was concerned chiefly with rather simple cases which could be treated theoretically with some degree of exactness rather than those which actually occur in practice   Indeed, from the author's point of view that the FeO content of the metal is an indispensable factor, there was nothing else to be done since the only available data on open-hearth reactions, at the time of writing, which included any sort of analytical determination of this quantity, were in the two runs reported by Herty and his coworkers, mentioned on page 95

The reference to Mr Styri's early equation for the reaction velocity was made because as far as the writer had determined Mr Styri was the first to propose unimolecular equation for the carbon oxidation   However, the fact that Mr Styri is able to explain the observations on the actual course of the carbon elimination by mechanism somewhat different from any discussed by the author, and that Mr Dean, on the basis of still another mechanism, also obtained a unimolecular equation, only emphasizes the author's point that it is impossible to determine the true mechanism by which carbon is oxidized by studying the rate of carbon removal as it actually occurs under practical conditions

Mr Yap and Mr Bitzer seem to believe that the mechanism of a reaction can be determined from thermodynamic considerations   Unfortunately this is not true. Experience shows that thermodynamic considerations are generally unsafe guides in kinetic problems   In particular, it does not follow that because the thermodynamics proves that a certain substance, such as Fe_3C, predominates in concentration over another, such as carbon, the rate determining reaction must involve the substance in the higher concentration   Thus one cannot say, with assurance, that Fe_3C is or is not a factor in determining the rate of carbon oxidation from considerations of its free energy or heat of formation, nor from the free energies or heats of reaction with FeO   Unfortunately, the measurements of reaction velocity will not distinguish between carbon and Fe_3C in reactions A and C, as has already been mentioned (p 85)

The fourth possibility (p. 86), which Mr. Yap prefers, was eliminated on the basis of the heretofore generally accepted assumption that Fe_3C was very highly dissociated at 1600° C   Should this assumption be disproved and it be established that both Fe_3C and carbon react independently with FeO, it is still possible to treat the problem theoretically by modifying equation 5   Independence of rates means merely that a reaction velocity equation characteristic of each reaction may be set up; the concentration terms involved in the two equations may, and, in this case, would be, interdependent   Experimentally, however, such a situation is extremely difficult and perhaps impossible to solve   Few cases have been studied in which two substances whose relative concentrations are determined by an equilibrium relation interact with a common third substance or in which the total rate was determined by some combination typified by reactions B and A or B and C with the remaining reaction C or A individually faster than the other two   The determination of the individual velocity constants in such cases depends generally upon some special

feature of the system [38]   If this fourth possibility should be the correct one, the total rate of carbon elimination will be governed by two of the three reactions A, B and C, but unless there is some particularly fortunate interrelationship or experimental procedure available it will probably be impossible to determine experimentally the correct values for the individual rate constants

Mr Reinartz, Mr Bitzer, Mr Styri and Mr Kinzel have brought out a number of points of practical importance, among which are included slag composition and properties, the reactions within the slag layer, the furnace atmosphere which depends in part upon furnace design and fuel characteristics, and the character of the initial charge   While certain parts of each of these could be discussed theoretically, it would not seem profitable to do so at present in view of the large number of difficulties already encountered in the theoretical treatment and the lack of pertinent quantitative data   The lack of information and quantitative data which would enable an investigator to have some reasonable assurance that the detail to be discussed is of genuine practical importance and not merely a minor side issue is perhaps the most serious difficulty   Much experimental work is needed before satisfactory conclusions can be drawn

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[38] As an example, see the work on the reactions of iodide ion and tri-iodide ion with persulfates [Jette and King· *Jnl* Amer. Chem Soc (1929) **51,** 1034, 1048]

The Carbon-oxygen Equilibrium in Liquid Iron*

By H C Vacher† and E H Hamilton,‡ Washington, D C

The limiting concentrations of carbon and oxygen which may co-exist at equilibrium in liquid iron are important in determining the degree to which liquid steel may be refined before it is deoxidized.   Most refining processes depend upon the oxidation of a highly carburized iron which invariably results in contaminating the steel with oxygen   The oxygen thus introduced presents many problems to the refiner, who in turn has attempted to rid the steel of this impurity by deoxidation with elements such as manganese, silicon and aluminum   The importance of the limiting concentrations of carbon and oxygen is accentuated in view of a number of recent researches which have indicated in many instances the existence of relations between oxide inclusions and dissolved oxygen and physical properties and chemical behavior of steel   The determination of the equilibrium concentrations of carbon and oxygen existing in iron under steelmaking conditions is obviously of fundamental importance.

It has been generally assumed that the product of the equilibrium concentrations of carbon and oxygen in liquid iron is a constant and that this product is directly proportional to the carbon monoxide pressure in equilibrium with the liquid iron   Herty[1,2] has computed values for this product based on open-hearth data which are all in the neighborhood of 0 01 to 0 03 (per cent. FeO × per cent. C) for temperatures in the vicinity of 1550° to 1600° C and one atmosphere pressure   Kinzel and Egan[3] have attempted to determine the value of this product by exposing liquid iron to carbon monoxide at one atmosphere pressure   The value reported by them was 0 0005 at 1550° C.   In order to apply certain equations to the rate of carbon elimination in the open-hearth process, Feild[4] found it necessary to assume a value of 0 0102 at 1580° C for this

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[1] C H Herty, Jr et al   The Physical Chemistry of Steel-Making   The Solubility of Iron Oxide in Iron   Min & Met Invest *Bull* 34, U. S Bur Mines, Carnegie Inst of Tech and Mining and Metallurgical Advisory Boards (1927)

[2] C H Herty, Jr Discussion   Iron and Steel Technology, A I M E (1928) 131

[3] A B Kinzel and J J Egan Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron   *Trans* A I M E , Iron and Steel Div. (1929) 304–319

[4] A L Feild Rate of Carbon Elimination and Degree of Oxidation of the Metal Bath in Basic Open-hearth Practice.   Iron and Steel Technology, A I M E (1928) 114–130.

product   Recently, Larsen[5] has computed this product as being 0 0016 at 1600° C   He concluded, however, that this value may be in error by 1000 per cent or more   Many computed values for this product have been reported previous to those mentioned above   However, the many assumptions involved and the unreliability of the data then available make these values extremely doubtful   The values given by Herty and by Kinzel and Egan for the carbon-iron oxide product are probably the most reliable, as they represent values from data directly obtained from liquid iron   The large difference between these values (0 010 to 0 030
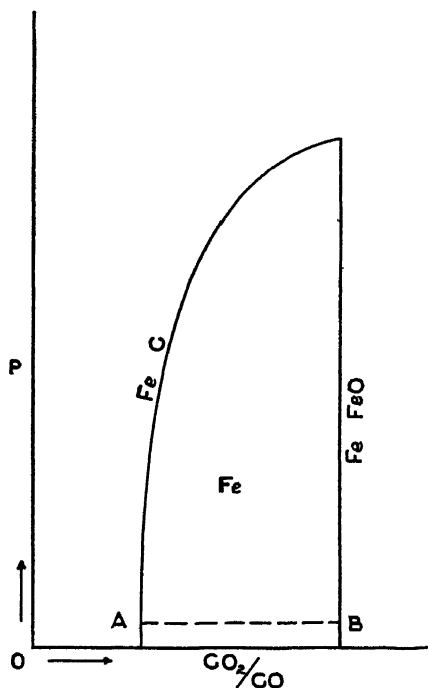
FIG 1 —PRESSURE-COMPOSITION DIAGRAM FOR LIQUID IRON AND CARBON OXIDES

and 0.0005) makes it necessary to do more work in order to establish better the value of this product

In the present work the attempt has been made to determine the value of the carbon-oxygen product over a wide range of concentrations at a constant temperature and one atmosphere pressure of carbon oxides. The problem as a whole is probably best illustrated from the diagram in Fig 1.   The enclosed area represents the pressures and composition of the carbon oxides which can be in equilibrium with a solution of carbon and oxygen in liquid iron at a given temperature   The boundary line

[5] B M Larsen Origin and Effect of Inclusions in Steel *Metals & Alloys* (1930) 1, 763–769

at the left represents the pressures and compositions when the solution is saturated with carbon, whereas the line at the right represents the solution saturated with oxygen   The two lines begin with iron solutions saturated respectively with carbon and oxygen at zero pressure of carbon oxides.   They intersect at a pressure and composition of carbon oxides which are in equilibrium with a saturated solution of carbon and oxygen   The solubilities of carbon and oxygen in liquid iron at 1600° C. are about 5 5 per cent. and 0 3 per cent., respectively.   The composition of the carbon oxides at any pressure in equilibrium with iron saturated with carbon may be computed from the equilibrium constant of the reaction

$$CO_2 + C = 2CO; K_1 = P \frac{p^2(CO)}{p(CO_2)} \quad [1]$$
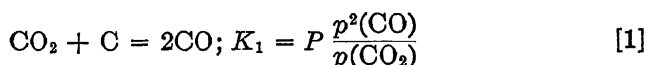
whereas the composition at any pressure for iron saturated with oxygen is determined by the equilibrium constant of the reaction

$$FeO + CO = Fe + CO_2; K_2 = \frac{p(CO_2)}{p(CO)} \quad [2]$$
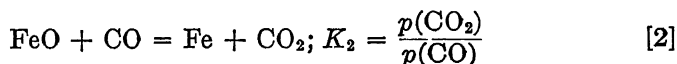
It is therefore, possible, given values for K_1 and K_2 at 1600° C., to compute the partial pressures of the carbon oxides and thereby the total pressure in equilibrium with an iron solution saturated with carbon and oxygen   The value of K_1 at a given temperature may be computed from the equation

$$\log K_1 = -\frac{8932}{T} + 2.45 \log T - 0.00108T + 0.00000011T^2 + 2\ 76$$

This equation is derived from the relation

$$\Delta F_T{}^\circ = -RT\ln K$$

and the free energy equation given by Lewis and Randall[6] for reaction 1   The value of K_2 may be computed from a similar equation given by Garran[7] for reaction 2.

$$\log K_2 = \frac{4160}{T} + 9\ 51 \log T - 0.00121T - 31.68$$

These equations represent equilibria data at temperatures in the vicinity of 900° C.   However, assuming that the discontinuities throughout the extrapolated temperature range are not large and may be disregarded, these equations may be considered as giving fair values for K_1 and K_2 at steelmaking temperatures.   The equations

$$FeO + C = CO + Fe \text{ and } K_{(3)} = K_{(1)} \cdot K_{(2)} = p_{(CO)} \quad [3]$$
$$2FeO + C = CO_2 + 2Fe \text{ and } K_{(4)} = K_1 \cdot K_{(2)}{}^2 = p_{(CO_2)} \quad [4]$$
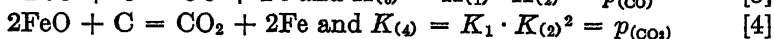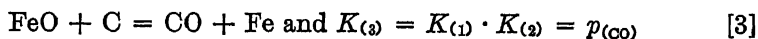
    [6] G. N. Lewis and M. Randall: Thermodynamics and the Free Energy of Chemical Substances, Ed. 1, 574.   New York, 1923.   McGraw-Hill Book Co
    [7] R. R. Garran: Equilibria at High Temperatures in the System Iron-Oxygen-Carbon.   *Trans.* Faraday Soc (1928) **24**, Pt. 3, 201

represent the partial pressures of carbon monoxide and carbon dioxide respectively, in equilibrium with carbon, iron oxide and iron and therefore in equilibrium with the soluble constitutents of the iron phase. These equations are obtained by combining reactions 1 and 2 The values for K_1 and K_2 at 1600° C have been computed from these equations and are 23,529 and 0 25 respectively The partial pressures, therefore, in equations 3 and 4 are approximately 6000 and 1500 atm respectively, thereby giving a total carbon oxide pressure of 7500 atm in equilibrium with a solution containing 5 5 per cent carbon and 0 3 per cent oxygen at 1600° C A solution of carbon and oxygen in liquid iron in equilibrium with carbon oxides at one atmosphere and 1600° C. therefore, may be represented in Fig. 1, by the line AB. At A, the composition of the carbon oxides is obtained from the equation given for reaction 1 as 99.994 per cent. carbon monoxide and 0 006 per cent. carbon dioxide, and is in equilibrium with the saturated solution containing about 5 5 per cent. carbon and a low percentage of oxygen. An experimental determination indicated that the percentage of oxygen was less than 0 003 per cent. The ratio of carbon oxides and thus the percentage composition at B has already been given as 0.25 (K_2, reaction 2 at 1600° C.) This composition is in equilibrium with a solution containing 0.3 per cent oxygen and a low percentage of carbon. Analysis of highly oxidized iron indicates the carbon percentage as less than 0.01 At any constant pressure between the limits as indicated by the line AB, a change in gas composition would be accompanied by a change in composition of the liquid iron solution. The problem as a whole, therefore, is resolved into determining the concentrations of carbon and oxygen in the liquid iron solution and the corresponding composition of the carbon oxides over a wide range of composition at a given temperature and one atmosphere. The analytical methods available are not reliable for amounts less than 0 003 per cent. oxygen and 0 01 per cent. carbon, therefore the range of composition to be studied must be above these limits.

From consideration of means for determining the equilibrium concentrations of carbon and oxygen in the liquid iron solution, three methods of attempting to attain these concentrations were recognized. (1) Carbon may be added to a liquid iron solution of relatively high oxygen content, the gas pressure over the solution being kept at 1 atm. The solution is then solidified when the equilibrium concentrations have been attained and analyzed for carbon and oxygen. (2) Iron oxide may be added to a liquid iron solution of relatively high carbon content. (3) Liquid iron of varying carbon or oxygen contents may be exposed to carbon oxides of a given composition, for a time sufficient to attain equilibrium between the liquid iron solution and the carbon oxides The solution is then solidified and analyzed for carbon and oxygen.

In the first two methods, it is necessary to assume that the equilibrium concentrations are reached independently of the gas composition   The third method should be more satisfactory because the system as a whole would be in equilibrium and in addition would allow the gas composition to be correlated with the metal composition

The first series of experiments follows the first method, i e, addition of carbon to liquid iron having a relatively high oxygen content   The atmosphere for this series of experiments was kept at a carburizing composition by incasing the crucible in graphite which was at the same temperature as the liquid iron.   The loss of gas evolved during freezing in several cases led to the practice of killing these melts with silicon and in another series with aluminum   This method was deemed unsatisfactory for attaining equilibrium concentrations because of relatively large variations in the carbon-oxygen products thus obtained   These variations are doubtless due to the fact, already stated, that the liquid iron is not in equilibrium with the carbon oxides   The second method—the addition of iron oxide to high-carbon iron—was not tried, as it would have the same disadvantage   Work was continued employing the third method.   In this method the liquid iron charge was prepared to have initial carbon and oxygen concentrations corresponding to a lower pressure of carbon oxides than was used in the experiment   This was accomplished by a preliminary melting in a vacuum   The charge was then held molten while a mixture of carbon oxides of predetermined composition was introduced into the vacuum until a pressure of 1 atm. was reached   The molten sample will attain equilibrium by reacting with the carbon oxides, the resulting concentrations of carbon and oxygen depending upon the composition of the carbon oxides   Thus, by varying the composition of the carbon oxides, relatively high oxygen or high carbon values can be obtained in the liquid metal.   Results obtained with this method were more consistently uniform than those obtained from the first method   Details of the two series of experiments by these two methods were as follows:

A high-frequency induction furnace such as is used in the vacuum fusion method for determining oxygen in steel was employed in these experiments   The crucibles were made from precalcined pure magnesia, moistened with a 2 per cent. solution of magnesium chloride ($MgCl_2 - 6H_2O$)   The crucibles were made by tamping the magnesia around a suitable mandrel in a graphite shell and then calcining at 1750°C   The temperature measurements were made with an optical pyrometer.   In order to be assured that the pyrometer readings taken on the liquid iron near the crucible wall were correct, readings were taken as an iron sample melted and compared with the accepted melting point of iron   For the first series of ingots where the crucible was contained in a graphite shell, these readings agreed with the melting point of iron   Therefore, it was

TABLE 1 —*Composition of Material Used in Preparing Ingots*

Identification	HCl Residue Alumina, Per Cent	Oxygen, Per Cent	Carbon, Per Cent	Manganese, Per Cent	Sulfur, Per Cent	Silicon, Per Cent	Aluminum, Per Cent
SI-4, ingot iron	0 0014	0 075					
SI-2, ingot iron	0 0019	0 065	0 05	0 03	0 023	nil	
Fe-C alloy		< 0 002	5 0				
Fe-Al alloy	0 062						6 8

TABLE 2 —*Carbon-oxygen Products Obtained by Addition of Solid Carbon to Liquid Iron*

Ingot No	Carbon Added, Per Cent	Carbon, Per Cent	Final Composition of Iron Ingot		Carbon-oxygen Product	Duration of Heating after Addition of Carbon, Min
			Oxygen by Vacuum Fusion, Per Cent	Oxygen by HCl Residue, Per Cent		
UNKILLED INGOTS, 1580° C						
1	0 2	0 29	0 019		0 006	60
3	0 3	0 32	0 018		0 006	65
4	?	0 27	0 028		0 008	60
5	none	0 20	0 005		0 001	60
27	none	0 09	0 008		0 001	
28	none	0 10	0 007		0 001	
29	0 7	0 68	0 008		0 005	15
30	0 6	0 61	0 013		0 008	15
SILICON-KILLED INGOTS, 1580° C						
8	0 05	0 27	0 013		0 0035	75
12	none	0 20	0 013		0 0026	30
13	0 10	0 27	0 011		0 0030	30
14	0 20	0 32	0 010		0 0032	30
15	0 05	0 14	0 021		0 0029	< 5
16	0 37	0 66	0 009		0 0059	30
17	0 60	0 67	0 007		0 0047	15
18	0 70	0 79	0 003		0 0024	15
ALUMINUM-KILLED INGOTS, 1600° C.						
21	none	0 05		0 018	0 001	15
22	0 10	0 23	0 012	0 008	0 003, 0 002	15
23	0 20	0 27		0 010	0 003	15
24	0 20	0 27		0 005	0 001	15
25	0 30	0 34		0 019	0 006	15
26	0 40	0 38	0 004	0 014	0 0015, 0 005	15

assumed that subsequent readings at higher temperatures would be correct   For the second series of ingots where the sample itself furnished the only source of heat the readings did not agree with the melting point of iron, thereby making it necessary to apply a correction.   At a temperature of 1620° C. this correction amounted to 95°.   Analyses of the materials used in these experiments are given in Table 1

First Series of Ingots

Experimental ingots were prepared by adding varying amounts of carbon, either in the form of an iron-carbon alloy or in the form of small pieces of Acheson graphite, to from 40 to 100 grams of molten iron (SI-2, Table 1) which was relatively high in oxygen   Before the charge was melted, the furnace was evacuated and carbon dioxide admitted to a pressure of 1 atm.   The hot graphite encompassing the crucible and charge was relied upon to reduce the carbon dioxide to a carburizing mixture of carbon oxides   After the addition of carbon the metal was maintained molten long enough to reach equilibrium.   Fifteen minutes was sufficient, as shown by Table 2.   After 15 or more minutes, the power was shut off and the iron allowed to freeze in the crucible   The resulting ingot was analyzed for carbon by the ordinary combustion method and for oxygen by the vacuum fusion method   In this way a series of ingots was prepared and the value of the carbon-oxygen product was calculated (Table 2)   Where boiling did not occur, ingots 1, 3, 4, 29 and 30, the values are believed to be most reliable.   The average of these values is 0 0066   The temperature for these experiments was 1580° C.   Boiling occurred in this series if the carbon content of the melt was between 0.04 and 0 3 per cent.

It appeared that boiling during solidification might be overcome by adding small amounts of silicon or aluminum just prior to freezing   Results for ingots to which silicon had been added are given in Table 2.   The temperature for this series of melts was 1580° C   The values for the carbon-oxygen product are more uniform but somewhat lower than in the unkilled ingots   However, the values for oxygen for this series are believed to be low because of the escape from the melt of insoluble oxides formed when the silicon was added.   Immediately after the silicon was added, it was observed that particles were either forming on the surface of the melt or rising from the interior and moving towards the crucible walls   The results indicate the latter condition.

The ingots to which aluminum, in the form of an iron-aluminum alloy, was added were made in a slightly different apparatus.   This consisted of a graphite crucible and cover, fitted with a graphite chimney, packed in an induction coil with loose magnesia sand.   The upper end of the chimney was open to the air at all times.   The crucible containing the charge was placed in this graphite shell prior to assembling and the

charge was melted and kept molten at 1600° C.   The addition of carbon, and later of iron-aluminum alloy, was made through the chimney   The analyses of these ingots are given in Table 2   The oxygen analyses were made by determining the alumina by the hydrochloric acid residue method.   A wide range of values for the carbon-oxygen product was obtained, indicating that all of the oxygen had not been converted to alumina in some of the melts   This was verified by analyzing two of these ingots for oxygen by the vacuum fusion method.   The analyses showed a higher value than the residue method for an ingot giving a low carbon-oxygen product and a lower value for an ingot giving a higher product   It appears, therefore, that the low products obtained for these ingots are more liable to error due to errors in the oxygen determination than are the higher products   The carbon-oxygen products from ingots 25 and 26 are considered as the best of the aluminum-killed ingots.

The carbon-oxygen products obtained from unkilled ingots which did not evolve much gas in solidifying possibly represent equilibrium concentrations   However, the variations in results for this series of unkilled ingots are too great to be satisfactory.   These variations appear to be greater than can be attributed to possible errors in the analyses of carbon and oxygen   Products from the silicon-killed ingots are all likely to be low, because of the escape of insoluble oxides   The products obtained from the aluminum-killed ingots may be low on account of incomplete precipitation of the oxygen by the aluminum, although it was shown that in two high products precipitation may be complete.   The average of the carbon-oxygen products thought to be reliable from the aluminum-killed ingots are of the same order of magnitude as the average from the best unkilled ingots   The difference of the two averages may be due to the difference in temperature.   In an attempt to obtain smaller variations in the carbon-oxygen products, a second series of ingots was made, using the third method of attaining equilibrium, i. e , exposing liquid iron to a known mixture of carbon oxides.

Second Series of Ingots

The final composition of the metal samples in this series was determined by the composition of the carbon oxides in contact with the liquid iron   The composition of the gases was determined by controlling the temperature of a tube of granular charcoal through which the gases were circulated.   After passing through the hot charcoal the gas passed over the surface of the melt, thus insuring a constant atmosphere over the metal.   The apparatus is shown in Fig 2   The train is flushed out by admitting carbon dioxide at H and letting it escape at J.   After this has been completed the gas is circulated by means of a small mercury plunger pump D through the tube resistance furnace C containing the granular charcoal until the gases have attained a constant composition.

The gases then are circulated through the furnace, across the surface of the melt, which is kept at 1620° C , and then back to the charcoal furnace C This circulation through the furnace was maintained after it had again
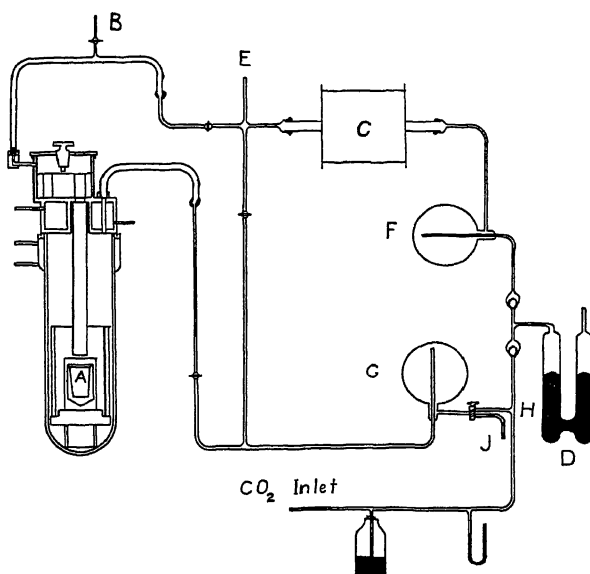
Fig 2.—Arrangement of apparatus for preparation of second series of ingots melted under carbon oxides of known composition.

Table 3 —*Carbon-oxygen Products Obtained by Exposure of Liquid Iron to Carbon Oxides of Known Composition at 1620° C*

Ingot No	Gas Composition, CO_2, Per Cent	Initial Composition of Iron Charge		Final Composition of Iron Ingot				Carbon-oxygen Product	Duration of Heating after Addition of Carbon, Min
		C, Per Cent	O$_2$, Per Cent	Al, Per Cent	C, Per Cent	By Vacuum Fusion Method, O$_2$, Per Cent	By Al$_2$O$_3$ Residue Analysis, O$_2$, Per Cent		
S-50	1 1	1 50	Tr	3 9	0 94		0 003	0 0028	85
51	2 0	1 50	Tr	5 3	0 51		0 006	0 0031	85
56	0 5	0 05	0 065	3 9	0 25		0 011	0 0027	125
54	2 1	0 05	0 065	0 85	0 10		0 022	0 0022	80
36	6 7	Tr	0 046		0 039	0 068		0 0027	47
35	8 2	Tr	0 046		0 024	0 106		0 0025	90
52	8 7	0 05	0 065		0 019	0 128		0 0024	80
55	9 2	0 05	0 065		0 016	0 125		0 0020	120
42	11 3	0 47	0 008		0 015	0 155		0 0023	60
44	7 7	0 47	0 008		0 013	0 133		0 0017	50
38	10 0	0 26	Tr		0 013	0 196		0 0025	45

attained a constant composition for the lengths of time shown in Table 3 A constant pressure of carbon dioxide was kept on the circulating gases The composition of the gases was determined from small samples taken

at *E*. At temperatures in the vicinity of 1100° C. a composition of less than 5 per cent. carbon dioxide could be easily attained. At lower temperatures considerable time was required before the composition became constant, thus making it difficult to obtain gas mixtures containing more than 5 per cent. carbon dioxide As a whole this method of controlling the composition of the carbon oxides is none too satisfactory for making precise mixtures

Before exposing the liquid iron to the carbon oxides, the iron was melted in a vacuum Fusion in a vacuum will reduce the amount of carbon and oxygen usually present in iron This is illustrated by analyses given in Table 3 The analyses of charges for ingots 35 and 36 represent the same material used for ingots 52, 54, 55 and 56, but after it had been vacuum-fused in an Arsem furnace

Liquid iron which had been in contact with carbon oxide mixtures containing less than about 7 per cent carbon dioxide boiled vigorously when freezing Therefore, when less than 7 per cent of carbon dioxide was present, approximately 5 g of aluminum was dropped into the melt prior to freezing The top portion of these ingots was almost entirely aluminum, as the time before solidification was not sufficient for thorough mixing This portion was cut off and the remainder used for carbon, aluminum and alumina analyses The presence of metallic aluminum showed that sufficient aluminum had entered the liquid iron to assure complete precipitation of the oxygen Carbon and oxygen values were computed with reference to the liquid metal before the aluminum was added

The results obtained from this series of ingots are given in Table 3 The data show that the carbon-oxygen products under these conditions are a constant, which is independent of the initial composition of the metal; of variations in time of exposure when time was greater than 45 min ; and of the composition of the carbon oxides. The average of these products is 0 0025 with a mean deviation of individual determinations from this average value of $\pm 0 0003$. Owing to the inaccuracies known to exist in the control of gas composition, the relation between gas composition and composition of the metal cannot be stated with accuracy It is evident, however, that the amount of the oxygen in the metal increases as the carbon dioxide content of the gas increases, and this relation holds up to at least 10 per cent carbon dioxide. Thus far, the results are in good agreement with the computed values given for the diagram (Fig 1)

SUMMARY

In the earlier stages of this work, values of 0 0066 at 1580° C. and 0.0055 at 1600° C. were obtained for the carbon-oxygen product. These results were obtained by the selection of values believed to be the best

of a series of experiments   The variation in this series, however, was so great as to cast some doubt on any result in the series.

Subsequent experiments, under better control, produced a value of 0 0025 for the product of the concentrations of carbon and oxygen in liquid iron at 1620° C. and 1 atm. pressure.   In obtaining this value it appears that the method of approaching equilibrium is sound, the elimination of the time factor (beyond 45 min) indicates that equilibrium was reached, and the same constant is obtained over a range of carbon content from 0.01 to 0 94 per cent. and of oxygen from 0 003 to 0 19 per cent   It is believed therefore, that the value 0 0025 at 1620° C approximates the true value for the product of the concentrations of carbon and oxygen in liquid iron solution that is in equilibrium with carbon oxides at 1 atm pressure.   This value expressed as the product of iron oxide and carbon is 0 011.   It appears to be of an order of magnitude quite different from the value 0.0005 at 1550° C obtained by Kinzel and Egan   It is within the range of Herty's computed values, 0 010 to 0 030 in the vicinity of 1550° to 1600° C., and is in good agreement with Feild's assumed value.   It is planned to continue this work at other temperatures and at lower pressures of carbon oxides

DISCUSSION

(G B Waterhouse presiding)

A B. KINZEL, Long Island City, N Y. (written discussion) —Previous results on this equilibrium constant as determined at the Union Carbide and Carbon Research Laboratories were reported last year [8]   In this work, an equilibrium constant of 0 0005 was obtained.   On hearing of the work at the Bureau of Standards, I visited the authors of this paper and discussed their work   There is no question as to the accuracy of the results or of the technique which they employed.   However, in view of the difference between their results and those we obtained, it was agreed to exchange samples and methods to see whether the cause of the discrepancy could be determined   The difference in the iron used, the difference in the crucible used, etc , proved to have no bearing on the result, but it is significant that one heat made by Vacher in an Arsem furnace, rather than in the induction furnace used for the rest of their work, gave results of the same low order of magnitude as those which we obtained previously. In view of the fact that the Arsem furnace arrangement is very similar to ours, this single result would seem to be more than fortuitous.   The difference then between the results obtained in the Arsem furnace and the induction must be accounted for by experimental conditions   Stirring of the metal in the induction furnace was suggested as a possible factor by Mr Vacher, but in view of the fact that in our previous work we believe that we approached equilibrium from both sides, this does not seem probable to us   The method of introducing the gas may affect the results, or it may be that there are two points of arrest in the iron oxide-carbon reaction, one giving a metastable equilibrium under certain conditions, with a constant of 0 01,

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[8] A B. Kinzel and J. J. Egan   Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron.   *Trans.* A I M. E , Iron and Steel Div. (1929) 304.

and the other giving equilibrium with a constant of 0 0005   The work which Herty has done in the open hearth shows rather definitely that the constant here reported by Vacher, rather than the 0 0005 which we obtained, is effective in the usual steel-making practice   If the conditions tending to the establishment of the lower constant could be determined, a way would be opened to possible improvements in the open-hearth practice

H STYRI, Philadelphia, Pa (written discussion) —If we calculate the product FeO $\times$ C from equation 3 for one atmosphere pressure of CO, using the data given in the paper, we obtain 0 0012, which is in line with previous theoretical values of this constant, but the result is about 10 times lower than the authors' experimental value   In order to find the reason for this it may be of help to get the complete data on the content of aluminum, silicon, manganese in all the material used in the experiments, because it may be possible that such elements affect the total oxygen content in the sample, if present in sufficient quantities

Considering the tests run under mixture of CO and CO_2, which apparently are the most reliable of the tests, several of these runs indicate that equilibrium was not reached   Thus, for instance, runs 51 and 54 ought to have the same carbon content and runs 35 and 44 also ought to have about the same carbon content, but in the reverse order of the values obtained   This result should be explained   It would be desirable to see check runs on this material in an atmosphere of pure CO

Kinzel did not report boiling in his tests [9]   It should perhaps have been of interest to see tests run under his conditions with additions of aluminum or silicon before cooling

J CHIPMAN, Ann Arbor, Mich (written discussion) —The second series of experiments not only yields consistent values for the carbon-oxygen product, but also provides a basis for explaining the marked discrepancies between the observed and calculated values for this constant   The many attempts that have been made to compute the values of this equilibrium constant have been defeated by the lack of two fundamentally necessary data—the heat of fusion of ferrous oxide and the activity of carbon in liquid steels   No real agreement between observed and calculated values can be expected until these uncertainties have been removed

It has been customary in calculations of this sort to assume that the activity of carbon is proportional to its mol fraction at all concentrations up to the saturated solution   The equally plausible assumption that the activity is proportional to the mol fraction of Fe_3C yields a final result which differs from the first by about 200 per cent   The activity of carbon in liquid steel could be calculated with a high degree of accuracy if precise data were available as to the concentrations of carbon dioxide and carbon monoxide in equilibrium with the steel   Although the authors state that the gas compositions given in Table 3 are known to be inaccurate, they are sufficiently consistent to permit at least an approximate calculation of the activity of carbon, with the understanding that the result may be subject to considerable modification when more accurate gas compositions are available.

The equilibrium between gases and metal is expressed by the following equation

$$C \text{ (in liquid Fe)} + CO_2 = 2CO; \quad K = \frac{p^2_{CO}}{a_C \times p_{CO_2}}$$
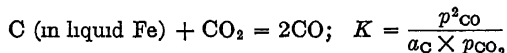
From this it is evident that the activity of carbon in the steel is proportional to the ratio p^2_{CO}/p_{CO_2} This ratio, which will be designated a', is given in column 2 of Table 4.   The ratio of a' to the mol per cent of carbon in the steel must (by Henry's law) approach a definite limiting value at low concentrations   This ratio, $a'/100N$,

[9] A B Kinzel and J J. Egan *Op cit.*

is tabulated in column 5   Excluding the first two values, which are obviously out of line with the others, the average value of $a'/100N$ is 120

In the saturated solution of iron in equilibrium with graphite the value of a' is numerically equal to the equilibrium constant in the reaction

$$C \text{ (graphite)} + CO_2 = 2CO, \quad K = \frac{p^2_{CO}}{p_{CO_2}}$$
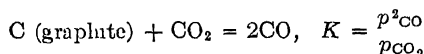
The experimental data on this reaction have recently been reviewed by Eastman,[10] who obtains an equation which appears to be superior to that of Lewis and Randall cited by the authors   Unfortunately Eastman's equation cannot be employed above

TABLE 4 —*Activity of Carbon in Liquid Steel at* 1620° C

CO, in Gas, Per Cent	a'	Carbon in Steel, Per Cent	Carbon, Mol Per Cent (= 100 N)	$\frac{a'}{100N}$
1 1	89 0	0 94	4 25	21
2 0	48 0	0 51	2 30	21
0 5	197 0	0 25	1 15	171
2 1	46 0	0 10	0 46	100
6 7	13 0	0 039	0 18	72
8 2	10 2	0 024	0 11	93
8 7	9 6	0 019	0 088	109
9 2	9 0	0 016	0 074	122
11 3	7 0	0 015	0 070	100
7 7	11 0	0 013	0 060	183
10 0	8 1	0 013	0 060	135
			Average	120

1600° K (1327° C)   This difficulty can be readily overcome by setting up specific heat equations which are valid at higher temperatures, and by employing the same equilibrium data that Eastman used.   The resultant equation, which is valid from 600° to about 2000° C is

$$\log K = -\frac{9277}{T} - 0\ 0755 \log T - 0\ 000218T + 9\ 845$$

The value of K at 1620° C , and hence of a' for the saturated solution by the above equation, is 19,200   The solubility of graphite in liquid iron at 1620° C is about 5 8 per cent, or 22 4 mol per cent   Therefore, $a'/100N$ is 857   This differs from the corresponding value in dilute solutions by a factor of about seven

The significance of this divergence is simply that the solution of carbon in iron is not ideal and cannot be treated by the laws of the perfect solution   If the activity is defined in the usual way by making it equal to the mol fraction of carbon in the very dilute solution, then in a solution of which the mol fraction is 0 224 the activity of carbon is approximately seven times this quantity   In an ideal solution the ratio of activity to mol fraction, of course, is constant at all compositions   Nonideal solutions of this type are common.   The case of thallium dissolved in mercury is a striking parallel.[11]

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[10] E D Eastman: The Free Energy of Water, Carbon Monoxide, and Carbon Dioxide   U S Bur. Mines *Inf Circ* 6125 (1929)

[11] G N. Lewis and M Randall *Op cit* , 267

Another valuable conclusion to be deduced from these considerations is that the product of the concentrations of carbon and iron oxide is not necessarily constant Indeed, in the saturated solution it may be only one-seventh as great as in dilute solutions, and it is noted that an equilibrium product one-seventh as large as that of Vacher and Hamilton would agree well with some of the calculated values for this constant   The question of how far into the range of concentrated solutions the equilibrium product will remain constant can be decided only by further experimental work   In this connection the activity of carbon, as calculated from precise determinations of the gas composition, will be essential to the thermodynamic interpretation of the results

E R JETTE, New York, N Y (written discussion) —In the following discussion, the writer attempts to present an impartial survey of the two recent determinations of this important constant by Kinzel and Egan (op cit) and by the present authors The determinations have been compared on all the points which seem essential, in the writer's opinion, to the accuracy of the value but based exclusively on the published work   The writer has been actively considering the experimental problem for some months and a number of the matters discussed below are as yet unsolved problems to him   He presents this discussion, therefore, partly in the interest of clarifying the present position of the value of the constant, and partly in the hope that the solution of some of his own experimental difficulties will develop as a result

In estimating the correctness of an experimentally determined equilibrium constant, four questions must be considered (1) Is the method used sound in principle? (2) Was the technique used adequate to secure results within the desired or stated limits of accuracy? (3) To what degree was equilibrium actually attained? (4) What interferences to reaching equilibrium were present, if any, and what side reaction might have affected the results? In the writer's opinion, of the results in Vacher and Hamilton's paper only those on the "second series of ingots" need to be discussed

Concerning the first question, the writer, at least, is satisfied as to the principle used by both investigators   In fact, when a rumor of the value obtained at the Bureau of Standards reached him some time ago, the writer began to work on the problem by Vacher and Hamilton's method of using definite gas mixtures and essentially Kinzel and Egan's furnace, except for minor details of control, etc   No results have yet been obtained, but preparations for the first run were virtually complete when Vacher and Hamilton's paper was received

The second question cannot be answered without more intimate information regarding the details   One of the most important points will be the method of determining the oxygen content and in comparing this latest work with that of Kinzel and Egan it is pertinent that the complete fusion method was used by both, although Vacher and Hamilton did obtain some results with the Al_2O_3 residue method   It is to be hoped that these two pairs of investigators will find some way of comparing their vacuum fusion techniques so that this point may be decided

The third question as to the completeness of attainment of equilibrium may be discussed in some detail   It is of fundamental importance that in both investigations the equilibrium was approached apparently only from the side where the product of the two concentrations was on the low side of the equilibrium value which each secures as the final result   At first sight it might seem that Vacher and Hamilton had started from the high side in the six ingots numbered 56, 54, 52, 55, 42 and 44, since the product for the first four of these original charges was 0 0032 and for the other two 0 0038   However, the charges were first melted in vacuo to reduce the carbon and oxygen present and the original carbon-oxygen product seems close enough to the final value so that the melting in vacuo would have reduced the carbon-oxygen product

at the moment of putting the furnace in the gas circuit to something below the final value   The data given are insufficient to be sure of this point   For the same reason, one cannot say with certainty whether Kinzel and Egan's run 3 was from the high or the low side

In discussing the final values found in both investigations, there are really two equilibria to be considered apart from the interfering processes which will be handled under question 4   These are the heterogenous equilibrium between gas and metal and the homogeneous one within the metal phase   The limited system under discussion is, in phase rule terms, three components in two phases   Therefore if total pressure, temperature and gas composition are fixed, the metal phase composition is also fixed   In Kinzel and Egan's experiment the gas composition was allowed to adjust itself   Gaines has calculated the CO_2 concentrations under these conditions to be about 0 5 to 1 per cent   It is important to note, therefore, that in Kinzel and Egan's run 3, where the original carbon content was 1 67 per cent, the final carbon was the same as when pure electrolytic iron was used   In Vacher and Hamilton's results 51 and 54, where the initial carbon concentrations were 1 5 and 0 05 per cent, the final carbons were 0 51 and 0 10 per cent respectively at practically the same ratio of CO_2 to CO According to Vacher and Hamilton's equation 2, the oxygen content of the metal should increase as the CO_2 percentage increases and yet comparing numbers 42 and 38 we find 0 155 and 0 196 per cent oxygen corresponding to 11 3 and 10 per cent CO_2 respectively   Similar though not so widely differing results are given for numbers 55 and 44   We should conclude from these observations that the internal evidence indicates that the equilibrium between gas and metal was somewhat more certainly established in Kinzel and Egan's investigation than in the other   One must not, however, decide too hastily that the same conclusion must be drawn for the equilibrium within the metal itself   In the absence of information on the rates of oxidation of iron by CO_2 and the reaction of FeO with carbon, the very great possibility exists that in the liquid metal phase the FeO and carbon react with sufficient velocity to keep that reaction practically at equilibrium, and the concordance of Vacher and Hamilton's results could, in fact, be taken as support for this view

It is to be noted that in neither investigation was there any satisfactory criterion of equilibrium applied during the course of a determination, but in both the system was held for a considerable period, from 1 to 2 hr , under the existing conditions after the available criteria were satisfied.

The criterion in Kinzel and Egan's work was the constancy of pressure read on an open monometer connected to the furnace   Variation in pressure within the furnace of a sealed system may be due to two causes, change of temperature and change of volume due to the chemical reaction   The temperature effect is difficult to estimate, since in the Sarbey furnace there are enormous temperature gradients in parts of the furnace and very small ones in others   If, however, we calculate the change in volume involved in the absorption of 0 03 per cent C from CO by 50 grams of iron and estimate the average temperature of the gas to be 100° in one case and 500° in another, we find that the change of pressure due to the chemical reaction would be 5 and 10 mm respectively   This, of course, is well within the sensitivity of any ordinary monometer   But if we calculate the temperature fluctuation necessary to produce these same pressure changes we find that a change in the *average* furnace gas temperature of 2° and 9° respectively would account for them   Kinzel and Egan attempted to control the temperature within 3° to 5°, especially towards the end, so that if the reaction were slow in coming to equilibrium the criterion would not be sufficiently sensitive to detect the final approach   Also, the criterion would not apply at all to three of their six runs, as these were made by flowing CO continuously through the

furnace It is perhaps significant that Kinzel and Egan's three most concordant results were obtained with the sealed furnace.

In Vacher and Hamilton's experiments, the criterion was *presumably* the constancy of gas composition. They state that gas was withdrawn from the system at point E which was *after* the gas from the high-frequency furnace had passed through the carbon tube. As a criterion of constancy of the gas composition over the molten iron, this procedure is practically useless It is to be emphasized, therefore, that both investigations have as the main support for the belief that equilibrium had been reached, first, the length of time subsequent to zero change in the criterion adopted and, second, the concordance of the various results among themselves It is evident that along these lines there is nothing to choose between the two investigations The same is true from the average deviations which for Kinzel and Egan's results give 8 5 per cent and for Vacher and Hamilton's 12 per cent. In the writer's opinion it is extremely unfortunate that neither of the investigators set the original conditions in some experiments so that the equilibrium could be approached very definitely from the high side.

When it comes to the fourth question, anyone who has not actually observed the experiments while they were performed is treading on dangerous ground. Nevertheless some of these possible interferences or side reactions must be brought up if only to obtain definite answers from the two investigators

The statement is made by Vacher and Hamilton that "liquid iron mixtures which had been in contact with CO_2 mixtures containing less than about 7 per cent CO_2 boiled vigorously when freezing " Kinzel and Egan report no such phenomenon, although their gas mixtures must have been considerably below this CO_2 content. Some elementary computations may serve to confuse the issue a little more. Let us assume that Kinzel and Egan actually had in their samples concentrations such as would give the constant 0 01 for [FeO] [C] but lost carbon and FeO during freezing so that the final product was only 0 0005. The amount of CO evolved during freezing may then be calculated for each one of their runs, with results ranging from 160 to 180 c.c , at the melting point and it will be assumed that all this was lost during the solidification It may be computed from the cooling curve given in their article, the specific heat of iron and its heat of fusion (Oberhoffer and Grosse value 65 4 cal per gram), that it required about 100 sec. for the entire sample to solidify Considering further that the volume of the sample was about 7 c c and the depth about 11 mm it seems difficult to believe that the liberation of 160 to 180 c c of gas would not have been observed and, in fact, one would expect to find the iron plastered all over the crucible walls! At least one would expect the ingot to be filled with blowholes It would be a matter of interest to have a report on this.

For the obvious purpose of accounting for Kinzel and Egan's low values, it might be suggested that the crucible walls took up a part of the FeO This would introduce another reaction and equilibrium into the system. If the oxidation of the iron by the gas phase takes place only a little faster, the crucible walls remove FeO, then the FeO content of the metal would be continuously below the true equilibrium value. In such a reaction the stirring action in the metal phase must play a vital part in this transfer of oxide from metal to crucible wall This line of argument is disposed of by the fact that the stirring in Vacher and Hamilton's experiments was certainly far greater than in Kinzel and Egan's Impurities reducible by iron or CO in the crucible walls and reoxidized after being dissolved in the iron could also conceivably account for low results. The substance most likely to be present in magnesia which would produce such an effect is silica. Again, when we consider the comparatively small area of contact and the slowness with which the reduced element would be transferred across the interface to the metal, there does not seem to be any great probability that this was a source of appreciable error in either case.

H C VACHER AND E H HAMILTON (written discussion) —The authors very much appreciate the interest in this paper evidenced by the discussions, which emphasize the fact that there is not yet a sufficient accumulation of satisfactory and concordant data to lead to a conclusion satisfactory to all   The discussion, however, will serve as an added stimulus to more work and may aid in recognizing and overcoming some of the experimental difficulties

We are not prepared to agree that the value 0 01 may represent a metastable equilibrium   In the work by Kinzel and Egan and in our work the constancy of the carbon-oxygen product has been used as a criterion of equilibrium   It is obvious that this criterion is not sufficient   A further and probably a conclusive criterion would be to determine the concentrations of carbon and oxygen within the iron as a function of the partial pressures of carbon monoxide and carbon dioxide   Data of this kind would permit theoretical considerations like those discussed by Dr Chipman   An accumulation of similar data on other gas-iron systems, such as Fe-H_2-O_2 system, would definitely prove or disprove the correctness of the present values for the carbon-oxygen product   Our work shows conclusively that such a function relating gas composition to liquid-metal composition does exist, whereas Kinzel and Egan made changes in their furnace procedure which would unquestionably affect the composition of the furnace gases, and found no corresponding change in concentration of carbon or of oxygen in the metal   The changes in furnace procedure were —the use of a closed furnace, the passage of carbon monoxide through the furnace, and the use of a crucible with a graphite cover   For this reason we believe that gas-metal reactions, necessary for the establishment of equilibrium, are relatively very slow in the furnace used by Kinzel and Egan and that the apparent decarburization and deoxidation shown by their results must be accounted for by outside reactions   This conclusion is supported further by our experience, as follows   It was found possible to keep a melt of electrolytic iron for 45 min in a carbon resistance furnace of the Arsem type and under one atmosphere monoxide without appreciably carburizing the iron (0 005 per cent)   Similar experiments with Armco iron, conducted in an induction furnace, showed carburization to the extent of 0 2 to 0 3 per cent   We believe this is explained by the fact that the metal is stirred in the induction furnace, thereby exposing a fresh surface of iron to the furnace gases, and that in the resistance type of furnace the metal is relatively without motion

The small amounts of silicon and aluminum which might be present in the iron, as pointed out by Dr Styri, are considered as not affecting the concentrations of oxygen, inasmuch as experiments with electrolytic iron have given carbon-oxygen products of the same order of magnitude as those given in the paper

Dr Jette's presumption that we used the constancy of gas composition as a criterion of equilibrium for an individual experiment is not correct   The gas was passed through charcoal to maintain it at a constant composition and was analyzed just before entering the furnace containing the liquid iron, in order to ascertain the composition of the gas which was impinging on the iron melt   There was no intention whatsoever of using this analysis as a criterion of the attainment of equilibrium between gas and liquid iron.

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A Thermodynamic Study of the Phasial Equilibria in the System Iron-carbon*

By Yap, Chu-Phay, New York, N Y
(New York Meeting, February, 1931)

Abstract

This is the first of a series of theoretical papers on the iron-carbon system   A simple critical analysis of the ordinary constitution diagram of the iron-carbon system yields valuable information regarding the nature of the equilibria in the liquid and solid states   It is shown, for example, that the solute in the melt is Fe_3C, but in solid γFe (austenite) the solute is carbon

The thermodynamic laws of the depression in the freezing point of solid solutions have been developed and discussed   Using the usual method of plotting the logarithm value of the concentration of the solvent (in this case, the ratio of concentrations of the solvent in the liquid and solid phases) against $1/T$, curves are obtained   A rigorous thermodynamic analysis of these curves has been shown to yield considerable information regarding the internal equilibria of the system, with which the phase rule does not deal altogether   In this way, it is shown again that the solute in the melt is Fe_3C, but in the solid γFe the solute is carbon

Various heats of reaction (fusion and transition) and other thermal data have been derived and discussed with a view to correlating the conflicting experimental data obtained by different investigators of the system

* This paper is available at the office of the Institute as *Technical Publication No 381*   Discussion is available in pamphlet form

Influence of Dissolved Carbide on the Equilibria of the System Iron-carbon*

By Yap, Chu-Phay, New York, N Y

(New York Meeting, February, 1931)

Abstract

This is the second of a series of theoretical papers on the iron-carbon system   The solidus lines obtained as a result of the different methods of investigation fall naturally into three classes, namely, (1) a straight solidus originally suggested by Roozeboom and supported in the main by the work of Carpenter and Keeling, Andrew and Binnie, et al , using the thermal analysis method, (2) a slightly curved solidus obtained by Honda and his associates, using the magnetic and resistance methods· and (3) Gutowsky's solidus obtained by the Heycock and Neville method of quenching at successively higher temperatures.

Although the thermodynamic method as shown in the first paper indicates that the straight solidus line is correct, no explanation has ever been advanced to account adequately for the disagreement in the shape and position of the solidus lines obtained.   The nature of the solute in austenite is theoretically discussed   On the basis of such discussions, the data obtained by Honda and Endo on the change of magnetic susceptibility of steels with respect to temperature were critically subjected to a graphical analysis, which is shown to yield a rational explanation of the curved solidus lines

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Inclusions and Their Effect on Impact Strength of Steel, I*

By A B Kinzel† and Walter Crafts,† New York, N Y.

Inclusions of nonmetallic matter have long been recognized as objectionable in steel. A complete theory of the effect of inclusions, which is consistent with that held today, was outlined in Howe's early work on the metallurgy of iron and steel   This, by analogy with wrought iron, assumes that the observed difference in properties between specimens with and across the direction of rolling is due to slag enclosures. The fact that wrought iron shatters in ballistic test is taken as an indication of the effect of inclusions on the resistance to shock. Since that time, the development of the metallurgical microscope has shown the discrete nonmetallic inclusions in the iron matrix   Better resolution has brought out the great number of inclusions, and the availability of good microscopes in steel mills and laboratories has constantly drawn more attention to these inclusions   This recent emphasis on inclusions has resulted in studies as to their nature, mode of formation and methods of elimination, such as the work of Wohrman, Dickenson, Herty and Schenk. In addition to the published works, many investigations which have not been published have been carried out by private laboratories and have resulted in the application of specifications intended to limit inclusions in many qualities of steel   Nevertheless, a clear understanding of the quantitative effect of inclusions on the physical properties of steel has been lacking.

It is the specific purpose of this study to determine the quantitative effect of inclusions on the physical properties of steel that determine its behavior under dynamic stress.   The study has shown that a quantitative relation between counted inclusions and impact strength does exist in normalized steels, but that factors other than readily visible inclusions are equally important.   Furthermore, the present commercial rating of inclusions is unreliable with respect to counted inclusions or dynamic tests, and this study indicates that the tensile-impact test is more reliable as a measure of quality.

General Scheme

The general plan of the study follows (1) To develop or establish a satisfactory measure of dynamic strength; (2) to develop or establish a

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satisfactory method of quantitatively measuring the inclusions, (3) to determine the relation of variation of dynamic strength to the variation of inclusions as measured, (4) to determine, by chemical methods, which if any of the types of inclusions present are most serious in affecting the dynamic strength, (5) to establish the relative importance of factors other than inclusions which affect the dynamic properties

On carrying out this scheme, it was found that the tensile-impact test and careful microscopic count gave results which were sufficiently accurate to determine the loss of shock resistance due to inclusions in the steels investigated   This reduction of strength was found to be large, and was materially influenced by the hardness of the material   Chemical analyses showed that the visible inclusion content and impact strength are proportional to a ratio of oxidic inclusions to the sulfur content   Furthermore, by means of inclusion analysis and vacuum fusion determination of oxygen, large erratic deviations in impact strength which are not due to visible inclusions have been found to be associated with nonmetallics, which are too small to be seen in the microscope or to collect on filter paper.

SELECTION OF MATERIALS

Although the writers would have preferred to work with plain carbon steels, it is evident that the hardness differential from center to surface of 2-in normalized bars would have been so serious as to preclude quantitative evaluation of the resultant figures   Accordingly, 2-in round and square bars of nickel steel containing 0.15 per cent carbon and 3-in round bars of chromium-vanadium basic open-hearth alloy steels containing 0 30 per cent. carbon were obtained from a standard commercial source Some of the material had actually been rejected because of the status of the inclusions, while other heats were selected because they were extremely clean, according to the standard commercial inclusion rating

In the system of notation that has been employed in order readily to identify the steels, the first digit refers to the heat and the second to the bar.   Thus, specimens 11, 12, 13, 21 and 22 are bars of nickel steel from two heats, and 31, 41, 51 and 52 are bars of the same material from three other heats   The former were 2-in. round, and the latter 2-in round-cornered square bars   Two specimens, A and B, were taken at random from each of the bars 31 to 52.   Specimens 61, 71, 72, 81 and 82 are 3-in round bars of chromium-vanadium steel.   Table 1 gives the detailed analysis of each bar and Fig. 3 shows the location of the specimens analyzed   All bars were normalized from 871° C (1600° F) to obtain uniformity.

MEASURE OF DYNAMIC STRENGTH

Measurement of dynamic strength is in itself a difficult problem when accurate and consistent values are desired.   The great difficulty in

duplicating results in the usual notched bar Izod, Charpy or similar tests, even with the greatest care in preparation of the specimens, is well known When longitudinal and transverse values are considered, interpretation of the results of such tests is very difficult   Our previous experience had shown that tensile-impact specimens give extremely good results when carefully prepared, therefore specimens of this type were used, with consistent results, as indicated by duplicate tests   A sketch of this type

TABLE 1 —*Chemical Analysis*

Speci-men No	C, Per Cent	Mn, Per Cent	P, Per Cent	S, Per Cent	Si, Per Cent	Ni, Per Cent	Cr, Per Cent	V, Per Cent
11	0 13	0 42	0 013	0 020	0 18	3 52	0 05	
12	0 13	0 41	0 013	0 018	0 16	3 53	0 06	
13	0 13	0 43	0 015	0 020	0 18	3 58	0 06	
21	0 16	0 53	0 014	0 021	0 24	3 53	0 05	
22	0 17	0 54	0 013	0 023	0 23	3 50	0 07	
31A	0 16	0 47	0 017	0 032	0 19	3 52	0 04	
B	0 16	0 48	0 019	0 038	0 20	3 54	0 04	
41A	0 15	0 45	0 010	0 018	0 20	3 41	0 01	
B	0 16	0 47	0 010	0 022	0 20	3 44	0 01	
51A	0 13	0 47	0 017	0 030	0 21	3 50	0 02	
B	0 16	0 47	0 012	0 025	0 22	3 50	0 02	
52A	0 14	0 44	0 017	0 021	0 18	3 44	0 02	
B	0 12	0 44	0 011	0 018	0 18	3 40	0 02	
61	0 31	0 66	0 017	0 025	0 25		0 90	0 15
71	0 36	0 64	0 017	0 030	0 15		0 88	0 13
72	0 31	0 60	0 014	0 022	0 11		0 81	0 13
81	0 33	0 73	0 018	0 026	0 28		0 95	0 13
82	0 37	0 74	0 020	0 025	0 28		0 95	0 13

of specimen is shown in Fig 1   As the diameter is small, care was taken to avoid any twisting of the specimen in machining, and the surface was ground with fine emery cloth to free it from circumferential scratches. No other special precautions were taken   The test was carried out on a standard 120 ft-lb Izod machine, the hammer being dropped from the full 120 ft-lb energy level in all cases

Specimens were taken from the centers of the bars and from midway between center and surface, in longitudinal and transverse directions, as shown in Figs 2 and 3.   Both the impact strength and elongation of each specimen were determined   Except in two cases, all values are the average of two tests, as shown in Table 2   From this, as well as from past work, the limit of accuracy in impact strength and elongation is considered to be approximately 5 per cent.   Although a few exceptional bars, such as No. 81, gave results that were outside the normal limit of

error, they cannot be considered as representative, for reasons to be mentioned later

For each grade of steel, the ratio between the impact strength and elongation is approximately a constant value. The difference between the ratio for the 0 15 per cent carbon nickel steel and the 0 30 per cent carbon chromium-vanadium steels is believed to be due largely to a differ-
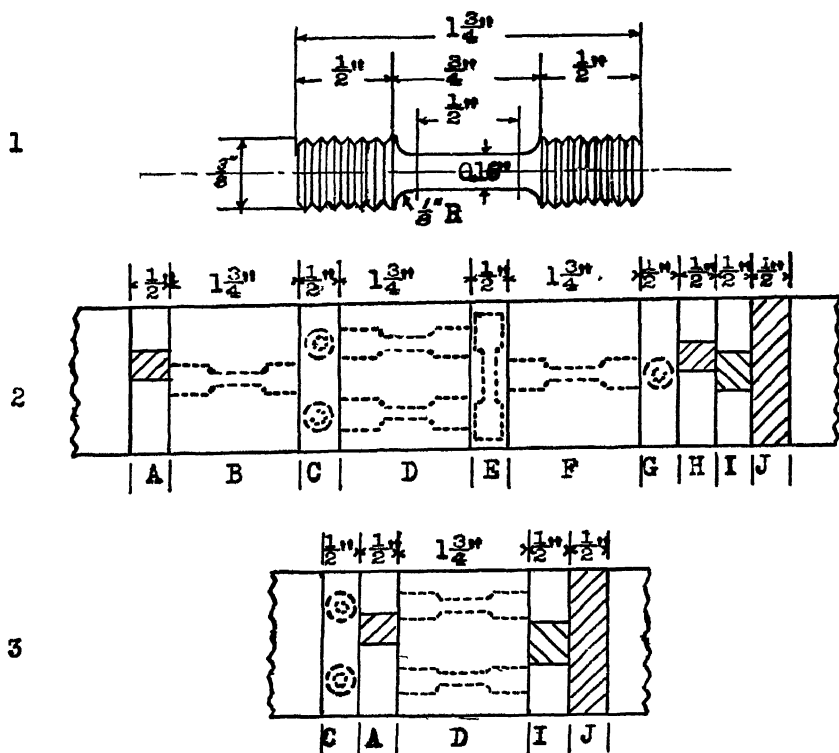
FIG 1—TENSILE IMPACT SPECIMEN
FIG 2—LOCATION OF SPECIMENS IN ROUND BARS
FIG 3—LOCATION OF SPECIMENS IN SQUARE BARS

A Micro for inclusion count.
B Tensile impact, center, longitudinal
C Tensile impact, midway, transverse
D Tensile impact, midway, longitudinal
E Tensile impact, center, transverse

F Tensile impact, center, longitudinal
G Tensile impact, center, transverse
H Micro for inclusion count
I Oxygen by vacuum fusion
J Turnings for analysis

ence in hardness, as the nickel steel had a hardness of approximately Rockwell B 80, and the chromium-vanadium approximately Rockwell B 90 This was further confirmed by a test on a bar of 0 45 per cent carbon steel, which had a hardness of Rockwell B 93 and which gave values in line with this hardness

Fatigue tests were also considered, but the difficulties in quantitatively evaluating inclusion effect in this test were believed to be very great

However, since the completion of the present work, such tests have been started at another laboratory on bars 31A to 51A

TABLE 2 —*Results of Tensile Impact Tests*

Specimen No	Location	Direction	Impact Strength, Ft-lb			Elongation, Per Cent in ½ In		
			1	2	Average	1	2	Average
11	Midway	Long	29 0	27 5	28 25	42 0	40 0	41 0
	Midway	Trans	24 5	25 5	25 0	34 0	36 0	35 0
	Center	Long	27 5	28 0	27 75	40 0	40 0	40 0
	Center	Trans	21 0	23 5	22 25	32 0	34 0	33 0
12	Midway	Long	28 0	29 0	28 5	40 0	42 0	41 0
	Midway	Trans	28 0	23 5	26 75	38 0	34 0	36 0
	Center	Long	28 5	28 0	28 25	40 0	42 0	41 0
	Center	Trans	24 0	26 0	25 0	34 0	36 0	35 0
13	Midway	Long	27 0	27 5	27 25	40 0	40 0	40 0
	Midway	Trans	28 5	26 0	27 25	38 0	38 0	38 0
	Center	Long	28 0	28 0	28 0	40 0	40 0	40 0
	Center	Trans	23 5	25 0	24 25	32 0	34 0	33 0
21	Midway	Long	30 0	30 0	30 0	38 0	40 0	39 0
	Midway	Trans	28 0	29 0	28 5	36 0	38 5	37 25
	Center	Long	29 5	28 0	28 75	40 0	38 0	39 0
	Center	Trans	25 0	25 5	25 25	32 0	36 0	34 0
22	Midway	Long	29 0	27 5	28 25	38 0	39 0	38 5
	Midway	Trans	26 0	27 0	26 5	32 0	34 0	33 0
	Center	Long	30 0	28 0	29 0	40 0	38 0	39 0
	Center	Trans	24 0	25 0	24 5	32 0	32 0	32 0
31A	Midway	Long	28 0	31 5	29 75	38 0	42 0	40 0
	Midway	Trans	27 5	27 0	27 25	34 0	36 0	35 0
31B	Midway	Long	32 0	25 5	28 75	42 0	32 0	37 0
	Midway	Trans	27 0		27 0	34 0		34 0
41A	Midway	Long	30 0	26 0	28 0	40 0	36 0	38 0
	Midway	Trans	25 5	21 5	23 5	32 0	30 0	31 0
41B	Midway	Long	28 0	24 5	26 25	32 0	32 0	32 0
	Midway	Trans	29 0	25 5	27 25	36 0	32 0	34 0
51A	Midway	Long	30 0	28 0	29 0	40 0	40 0	40 0
	Midway	Trans	28 0		28 0	36 0		36 0
51B	Midway	Long	27 5	31 5	29 5	36 0	42 0	39 0
	Midway	Trans	29 5	29 0	29 25	38 0	38 0	38 0
52A	Midway	Long	28 0	28 0	28 0	38 0	40 0	39 0
	Midway	Trans	25 0	26 0	25 5	32 0	38 0	35 0
52B	Midway	Long	29 0	29 5	29 25	40 0	40 0	40 0
	Midway	Trans	25 0	24 0	24 5	34 0	32 0	33 0
61	Midway	Long	27 0	30 0	28 5	32 0	34 0	33 0
	Midway	Trans	19 0	21 5	20 25	16 0	20 0	18 0
	Center	Long	31 0	28 0	29 5	36 0	30 0	33 0
	Center	Trans	24 0	21 0	22 5	24 0	20 0	22 0
71	Midway	Long	32 0	30 5	31 25	36 0	34 0	35 0
	Midway	Trans	23 0	25 0	24 0	24 0	26 0	25 0
	Center	Long	32 0	28 0	30 0	36 0	32 0	34 0
	Center	Trans	24 0	25 0	24 5	26 0	28 0	27 0
72	Midway	Long	33 0	29 0	31 0	36 0	32 0	34 0
	Midway	Trans	24 0	24 0	24 0	24 0	24 0	24 0
	Center	Long	29 0	28 0	28 5	32 0	30 0	31 0
	Center	Trans	24 5	25 0	24 75	26 0	28 0	27 0
81	Midway	Long	32 0	31 0	31 5	34 0	34 0	34 0
	Midway	Trans	22 0	15 0	18 5	22 0	12 0	17 0
	Center	Long	23 0	31 0	27 0	30 0	36 0	33 0
	Center	Trans	14 5	20 0	17 25	14 0	18 0	16 0
82	Midway	Long	34 0	33 0	33 5	32 0	32 0	32 0
	Midway	Trans	25 5	25 0	25 25	22 0	22 0	22 0
	Center	Long	32 0	27 5	29 75	32 0	28 0	30 0
	Center	Trans	22 0	23 5	22 75	20 0	20 0	20 0

ESTIMATION OF INCLUSIONS

Quantitative estimation of inclusion content was made by photographing a representative number of fields at a magnification of 50 dia The plates were then enlarged by projection on a screen, and the inclusions were counted with respect to length in brackets of graduated length The summaries of this count, expressed in number of inclusions of a given size per square millimeter, are shown in Table 3, in which the

TABLE 3 —*Results of Inclusion Count*

Speci-men No	Location	Length Brackets for Counting, Mm									Number of Inclusions per Sq Mm	Total Length of Inclusions, Mm per Sq Mm	Com-mer-cial Rating
		0 005 to 0 009	0 009 to 0 019	0 019 to 0 037	0 037 to 0 075	0 075 to 0 15	0 15 to 0 25	0 25 to 0 35	0 35 to 0 45	0 45 to 0 55			
		NUMBER OF INCLUSIONS PER SQUARE MILLIMETER											
1'	Midway	66 3	6 78	2 15	0 93	0 56	0 09				76 8	0 667	7 5
l1	Center	64 3	8 15	3 66	1 43	1 06	0 36	0 09	0 05		78 9	0 856	7 5
1	Midway	54 3	10 38	2 28	0 71	0 31					68 0	0 593	4 0
12	Center	54 6	7 87	1 95	0 93	0 65	0 05	0 05			66 1	0 624	4 0
13	Midway	60 0	8 19	2 35	0 87	0 34	0 06			0 03	71 8	0 641	10 0
13	Center	61 7	8 05	1 90	0 55	0 05					72 2	0 566	10 0
21	Midway	65 8	10 75	3 29	0 58	0 23	0 02	0 02			80 7	0 690	4 5
21	Center	63 3	11 10	2 78	0 65	0 49					78 3	0 686	4 5
22	Midway	59 2	7 26	1 60	0 43	0 09	0 03				68 6	0 537	2 5
22	Center	60 3	5 63	1 43	0 51	0 28					68 1	0 536	2 5
31A	Midway	31 3	7 64	2 35	1 11	0 44					42 8	0 450	3 3
31B	Midway	35 5	4 88	1 70	0 59	0 15					42 8	0 370	3 3
41A	Midway	65 7	8 00	2 37	0 44	0 30	0 08				76 9	0 638	8 8
41B	Midway	62 7	15 91	3 56	0 89	0 15		0 15			83 4	0 784	8 8
51A	Midway	47 4	6 53	1 56	0 30						55 8	0 432	3 0
51B	Midway	30 5	10 22	1 85	0 59	0 52					43 7	0 446	3 0
52A	Midway	57 8	8 15	2 96	1 33	0 59	0 15	0 08			71 1	0 716	7 0
52B	Midway	81 8	8 67	3 78	1 26	0 08					95 6	0 786	7 0
61	Midway	59 4	11 17	3 46	1 08	0 43	0 09				75 7	0 713	9 0
61	Center	51 1	11 76	4 26	1 44	0 43		0 05			69 0	0 702	9 0
71	Midway	47 1	8 93	2 41	0 52	0 09					59 0	0 501	8 0
71	Center	50 2	10 42	3 70	0 93	0 18	0 06				65 5	0 613	8 0
72	Midway	51 7	8 82	3 36	1 17	0 31	0 03				65 4	0 612	8 0
72	Center	49 5	10 61	3 64	1 11	0 43	0 06				65 3	0 643	8 0
81	Midway	63 0	12 68	6 38	2 68	1 45	0 15				86 3	1 022	3 0
81	Center	55 6	9 43	4 61	2 05	1 38	0 10				73 2	0 840	3 0
82	Midway	53 2	12 50	5 87	2 71	1 45	0 22	0 06			76 0	0 972	3 0
82	Center	55 6	12 78	6 24	2 53	1 05	0 06				78 3	0 906	3 0

number figure is the total number of inclusions per square millimeter, and the total-length figure is the sum of the lengths of all of the inclusions per square millimeter, as if they were placed end to end

Specimens were polished on the longitudinal section of a plane through the center of the bar, the whole section from one side to the other being used, although it was divided into two or three parts for ease in polishing

The polishing technique was that developed at these laboratories, in which all grinding and polishing up to the final stage is carried out on dry paper, and the final wet polishing with alumina on silk is reduced to a minimum. Past experience has shown that this method results in a quantitative retention of inclusions without exaggeration of their size caused by pitting around the inclusions. In addition, all specimens were etched with 10 per cent. aqueous chromic acid solution to darken the sulfides and make them more readily visible, as this etch does not attack the metal or any inclusions other than sulfides. Careful study of speci-
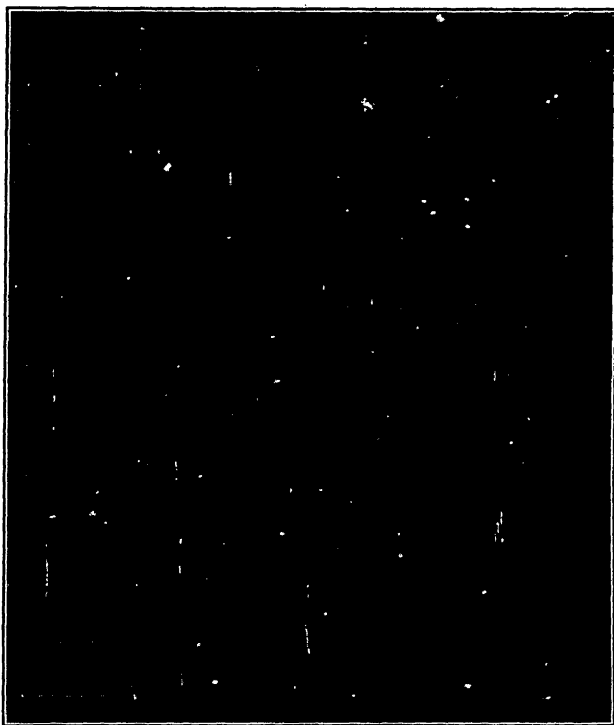
FIG. 4.—TYPICAL PLATE READY FOR INCLUSION COUNT.

mens before and after etching has shown that the apparent size of the inclusions is not affected. Should the sulfides be overetched, seepage of liquid occurs and is readily recognized.

The photographs were taken at representative predetermined locations, which were the same for each type of bar section. No attempt was made to select "average fields" and only a small deviation from the fixed positions was permitted in order to avoid imperfections in the specimen. Rectangular cross lines in the eyepiece divided the field into small squares to facilitate counting, and the exposure was timed to make all plates of uniform intensity. Fig. 4 shows a typical plate ready for

counting.   Two specimens from each bar were examined of samples 11 to
22 and 61 to 82, and one section each of specimens 31A to 52B   The
location of these specimens is shown in Figs 2 and 3 and the number
of fields and area covered in Table 4

TABLE 4 —*Area Covered in Inclusion Count*

Specimen No	Midway			Center		
	Number of Samples	Number of Fields	Total Area, Sq Mm	Number of Samples	Number of Fields	Total Area, Sq Mm
11	2	12	32 4	2	8	21 6
12	2	12	32 4	2	8	21 6
13	2	12	32 4	2	8	21 6
21	2	12	32 4	2	8	21 6
22	2	12	32 4	2	8	21 6
31A	1	6	13 5	1	4	9 0
31B	1	6	13 5	1	4	9 0
41A	1	6	13 5	1	4	9 0
41B	1	6	13 5	1	4	9 0
51A	1	6	13 5	1	4	9 0
51B	1	6	13 5	1	4	9 0
52A	1	6	13 5	1	4	9 0
52B	1	6	13 5	1	4	9 0
61	2	12	32 4	2	6	16 2
71	2	12	32 4	2	6	16 2
72	2	12	32 4	2	6	16 2
81	2	12	32 4	4	12	32.4
82	2	12	32 4	2	6	16 2

The detailed results of the inclusion count in Table 3 indicate that
no inclusions under 0 005 mm have been counted   The very great
number of small inclusions is apparent, and it is obvious that at higher
magnification many more very small inclusions could have been counted
with accuracy.   However, the area examined would have been much
smaller, and it was considered that the magnification employed would
give the most representative results   The inclusion count, therefore,
is restricted to inclusions over 0 005 mm. in length, and we must consider
the inclusions under this length together with the submicroscopic inclu-
sions.   Further work has justified this division, as shown by correlation
of impact strength with the "visible" or counted inclusions, and by the
agreement with chemical methods of inclusion analysis   For brevity,
the inclusions counted will be referred to hereafter as visible inclusions.
The great number of small inclusions is graphically illustrated in Fig. 5,
which shows the distribution of inclusions in an average specimen.

The choice of 50-dia magnification resulted from a consideration of the limitations and errors involved with various magnifications   This is the lowest magnification at which inclusions down to 0.005 mm. can be counted accurately, and at the same time is the highest magnification that gives a field large enough to include the relatively few large inclusions That a satisfactory balance is obtained may be seen from the distribution curve, in which both legs are approximately asymptotic.

The errors in this method of counting are reduced to the matter of sampling and the presence of spots caused by the optical system   Except
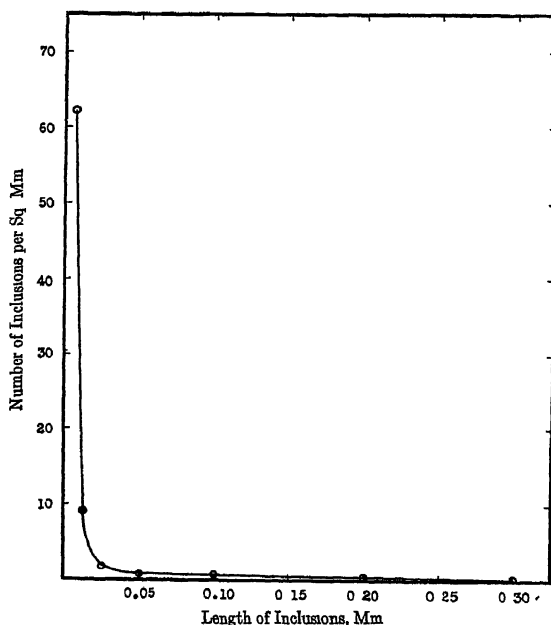
FIG 5 —TYPICAL DISTRIBUTION OF INCLUSIONS.

for 81, which was so erratic, even with extra samples, that no method of counting could give good results, the errors of sampling do not appear to be serious, and spots arising from the optical system can be eliminated almost entirely after sufficient experience. Although this method is unquestionably laborious, the accuracy of the results has justified the labor involved, and our experience indicates that the total error is less than with direct counting at the eyepiece. The latter entails a serious personal factor which is aggravated by the fatigue involved

In order to have a summary figure as a quantitative measure of the inclusions, the total number of inclusions per square millimeter and the sum of the lengths of the inclusions per square millimeter have been considered. The former varies largely with the small inclusions and is greatly affected by the arbitrary minimum length counted. As the num-

ber of small inclusions need not be proportional to the number of larger inclusions, the limitation of unit number as an index lies in the minimum length of the counted inclusions The value of this index is also affected by errors in counting the very small inclusions Total length, on
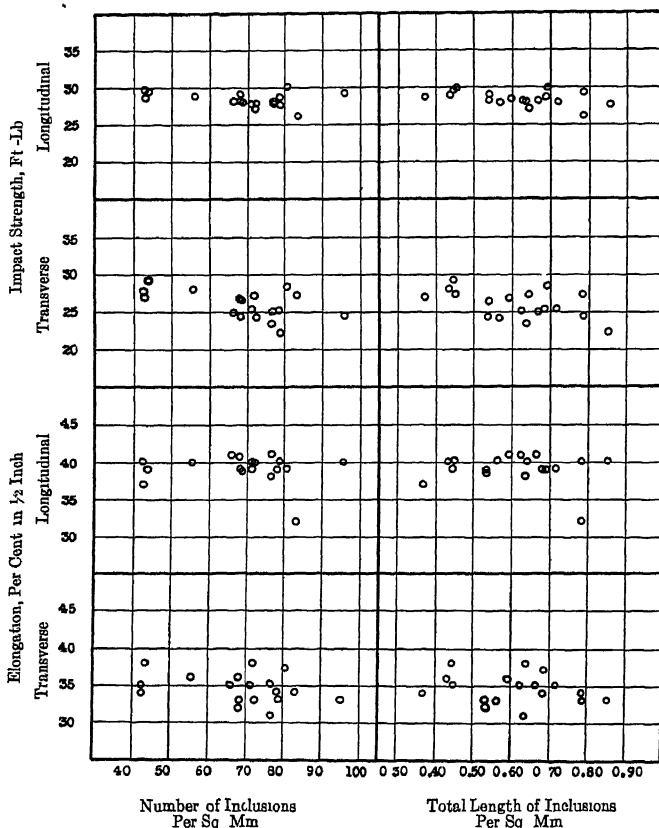
FIG 6 —EXPERIMENTAL VALUES, NICKEL STEEL, 0 15 PER CENT CARBON

the other hand, is not greatly affected by the small inclusions, but is weighted heavily by large ones As the number of large inclusions is small, the error in this case is largely due to sampling.

DIRECT CORRELATION OF VISIBLE INCLUSIONS WITH TENSILE-IMPACT PROPERTIES

In order to show graphically the effect of visible inclusions on the impact strength and elongation, these data have been plotted as shown in Fig. 6 for the 0 15 per cent carbon nickel steel, and Fig. 7 for the 0.30 per cent carbon chromium-vanadium steel A very noticeable loss of

impact strength and elongation with increased inclusions is evident.
Although this is not great in the longitudinal, it is pronounced in the trans-
verse tests   Moreover, in the softer steel the loss in the dirtiest steel
is approximately 25 per cent in transverse tests, whereas in the harder
steel this maximum loss amounts to about 50 per cent , which indicates
that the effect of hardness on the loss of strength due to inclusions is
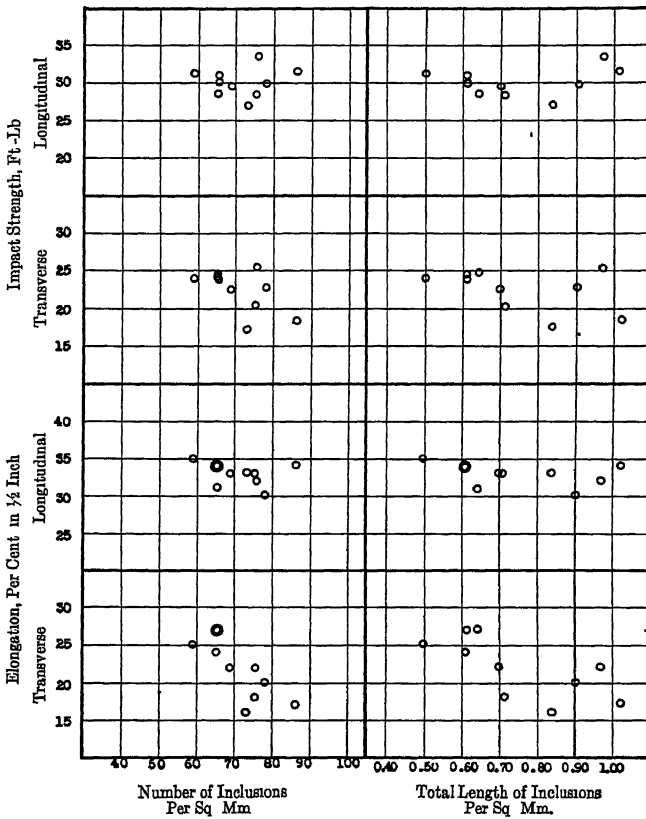
FIG 7.—EXPERIMENTAL VALUES, CHROMIUM-VANADIUM STEEL, 0 30 PER CENT CARBON

very great   It is apparent also that there is considerable variation from
the mean, and that some of this variation can be caused by experi-
mental error   However, some of the variation is well beyond the limits
of inaccuracy and must be attributed to other factors.

As the loss of impact strength and elongation is greater in the trans-
verse than in the longitudinal tests, the ratio between them is of interest
to show the widening gap with increased inclusion content. This is
illustrated in Fig. 8, which shows that together the steels form a con-
tinuous band. This band is wider if elongation rather than impact

strength is used as a measure, and indicates somewhat less accurate values for this measurement.

QUANTITATIVE LOSS OF TENSILE-IMPACT PROPERTIES DUE TO VISIBLE INCLUSIONS

In order to determine the quantitative effect of inclusions on impact strength, a factor has been determined, which, when multiplied by a value representing the inclusion content, results in the foot-pounds of impact strength or percentage of elongation loss due to the inclusions
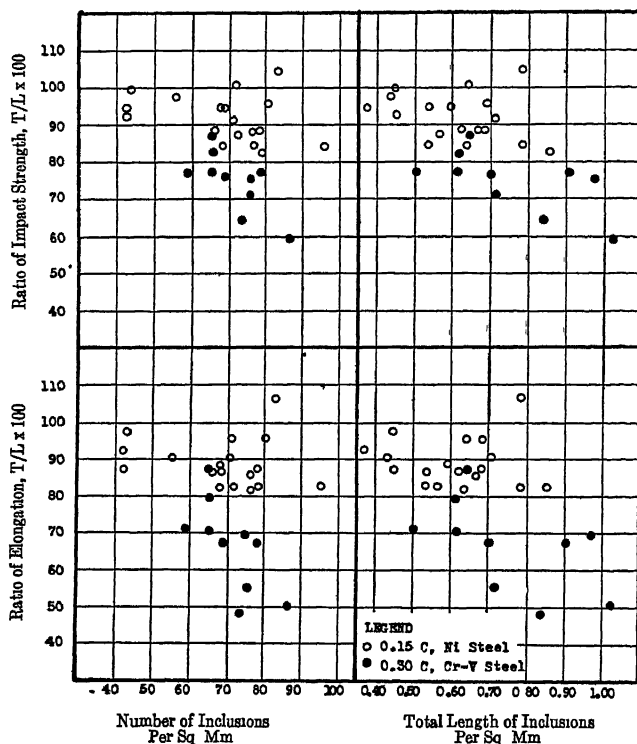
FIG 8 —EXPERIMENTAL VALUES, RATIO TRANSVERSE TO LONGITUDINAL

This loss is then added to the experimentally determined tensile-impact value to give a corrected value which the material would have if the inclusions or any factors that vary directly with the inclusions were absent. Accordingly, except for other factors, similar steels of a given hardness should give corrected values that are constant and independent of the inclusion count   Moreover, the ratio of transverse and longitudinal corrected values should be constant with respect to inclusions.

Correction factors were determined initially by the slope of the line derived from the differences in inclusion content and impact values between midway and center   For example, a uniform steel having no

difference between midway and center except the inclusion content will give differences between midway and center which, when shown graphically, will fall along a single line which would pass through the origin, such as *a* in Fig 9. With a constant difference between midway and center, the line would be parallel to the line mentioned above, and would

TABLE 5.—*Ratio of Impact Values, Transverse.Longitudinal* × 100

Specimen No	Location	Impact Strength, Ft-lb	Elongation, Per Cent in ½ In
11	Midway	88	85
11	Center	82	82
12	Midway	94	88
12	Center	88	86
13	Midway	100	95
13	Center	87	82
21	Midway	95	95
21	Center	88	87
22	Midway	94	86
22	Center	84	82
31A	Midway	92	87
31B	Midway	94	92
41A	Midway	84	81
41B	Midway	104	106
51A	Midway	97	90
51B	Midway	99	97
52A	Midway	91	90
52B	Midway	84	82
61	Midway	71	55
61	Center	76	67
71	Midway	77	71
71	Center	82	79
72	Midway	77	70
72	Center	87	87
81	Midway	59	50
81	Center	64	48
82	Midway	75	69
82	Center	77	67

cut the coordinates at points other than the origin, as in line *b* in Fig. 9, so that with commercial steels varying in properties between midway and center, the points fall in a band. The slope of the band then gives the proportionate loss of strength due to visible inclusions. These differences

are given in Table 6 and are shown graphically in Figs 10 and 11   It is obvious that in many cases the points are insufficient to establish a trend, but in some cases there is good agreement between the slope finally deter-
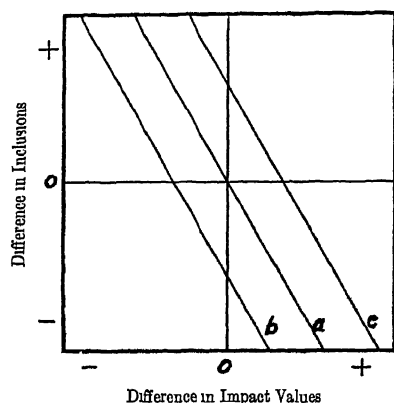
FIG 9 —THEORETICAL DIFFERENTIAL DIAGRAM

TABLE 6 —*Differences in Impact Properties and Inclusion Content*

Specimen No	Impact Strength, Ft-lb		Elongation, Per Cent in ½ In		Inclusions per Sq Mm	
	Long	Trans	Long	Trans	Number	Total Length
Midway Minus Center						
11	+0 50	+2 75	+1 00	+2 00	− 2 1	−0 189
12	+0 25	+1 75	0	+1 00	+ 1 9	−0 031
13	−0 75	+3 00	0	+5 00	− 0 4	+0 075
21	+1 25	+3 25	0	+3 25	+ 2 4	+0 004
22	−0 75	+2 00	−0 50	+1 00	+ 0 5	+0 001
61	−1 00	−2 25	0	−4 00	+ 6 7	+0 011
71	+1 25	−0 50	+1 00	−2 00	− 6 5	−0 112
72	+2 50	−0 75	+3 00	−3 00	+ 0 1	−0 031
81	+4 50	+1 25	+1 00	+1 00	+13 1	+0 182
82	+3 75	+2 50	+2 00	+2 00	− 2 3	+0 066
Specimen A Minus Specimen B						
31	+1 00	+0 25	+3 00	+1 00	0	+0 080
41	+1 75	−3 75	+6 00	−3 00	− 6 5	−0 146
51	−0 50	−1 25	+1 00	−2 00	+12 1	−0 014
52	−1 25	+1 00	−1 00	+2 00	−24 5	−0 070

mined and the location of the points   However, as the extrapolation is large, a great number of values would be needed to determine a trend accurately   Nevertheless, this method is of particular value, in that the use of differential values eliminates constant sources of error.

TABLE 7 —*Summary of Corrected Values, 0 15 Carbon Nickel Steel*

Inclusion Summary	Direction of Tests	Impact Strength, Ft-lb			Elongation in 2 In		
		Correction Factor	Mean Correction	Corrected Mean Imp Strength	Correction Factor	Mean Correction	Corrected Mean Elongation
Number	Long	1n = 0 03	2 07	30 5	1n = 0 03	2 07	41 1
	Trans	1n = 0 07	4 83	30 8	1n = 0 07	4 83	39 9
Total length	Long	1L = 3	1 85	30 3	1L = 3	1 85	40 9
	Trans	1L = 7	4 29	30 2	1L = 8	4 91	39 5
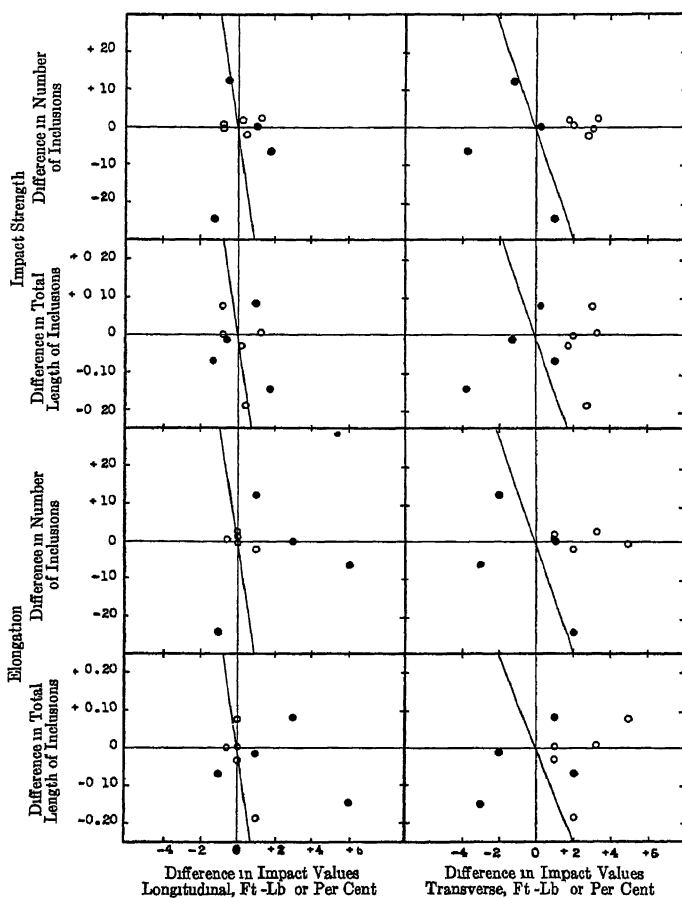
FIG 10 —CORRECTION FACTOR BY DIFFERENCES, NICKEL STEEL, 0 15 PER CENT.
CARBON

O = center minus midway
● = specimen *A* minus specimen *B*

After the correction factors were determined, as indicated above, they were corrected by trial until the corrected tensile-impact values and their transverse-longitudinal ratio were as constant with respect to inclusions as could be obtained with the data at hand. The correction values of nickel steels are summarized in Table 7 and are given in detail in Tables 8 and 9 and Fig 12. The corrected longitudinal values show some variation from the mean of 30 5 ft-lb., whereas the corrected
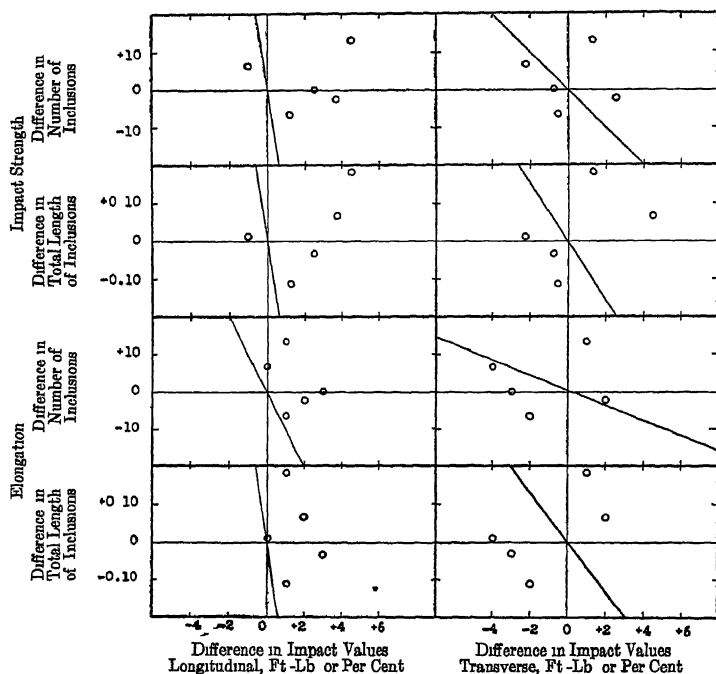
FIG 11—CORRECTION FACTOR BY DIFFERENCES, CHROMIUM-VANADIUM STEEL, 0 30 PER CENT CARBON

transverse values are comparatively erratic and there is considerable variation in the ratio between transverse and longitudinal values However, the mean value for the ratio approximates 100 per cent That this ratio is 100 rather than 80 per cent, or some other figure, indicates that there are no factors involved between transverse and longitudinal impact properties other than those which can be accounted for by the visible inclusions or factors varying directly with these inclusions

In general, the statements above that apply directly to the nickel steels apply to the chromium-vanadium steels; the corrected values are summarized in Table 10 and are shown in detail in Tables 11 and 12 and Fig. 13. However, these corrections leave something to be desired. It is apparent that in connection with heat 8 the results do not fit in

TABLE 8 —*Corrected Impact Values, 0 15 Per Cent Carbon Nickel Steel*
IMPACT STRENGTH CORRECTED BY NUMBER FACTORS

Spec-imen No	Location	Longitudinal			Transverse			Ratio Corrected Transverse / Longitudinal × 100
		Actual Impact Strength, Ft-lb	Correction Impact Strength, Ft-lb $1n = 0 03$ Ft-lb	Corrected Impact Strength, Ft-lb	Actual Impact Strength, Ft-lb	Correction Impact Strength, Ft-lb $1 n = 0 07$ Ft-lb	Corrected Impact Strength Ft-lb	
11	Midway	28 2	2 3	30 5	25 0	5 4	30 4	100
11	Center	27 7	2 4	30 1	22 2	5 5	27 7	92
12	Midway	28 5	2 0	30 5	26 7	4 8	31 5	103
12	Center	28 2	2 0	30 2	25 0	4 6	29 6	98
13	Midway	27 2	2 2	29 4	27 2	5 0	32 2	110
13	Center	28 0	2 2	30 2	24 2	5 0	29 2	97
21	Midway	30 0	2 4	32 4	28 5	5 7	34 2	105
21	Center	28 7	2 3	31 0	25 2	5 5	30 7	99
22	Midway	28 2	2 1	30 3	26 5	4 8	31 3	103
22	Center	29 0	2 0	31 0	24 5	4 8	29 3	95
31A	Midway	29 7	1 3	31 0	27 2	3 0	30 2	97
31B	Midway	28 7	1 3	30 0	27 0	3 0	30 0	100
41A	Midway	28 0	2 3	30 3	23 5	5 4	28 9	95
41B	Midway	26 2	2 5	28 7	27 2	5 8	33 0	115
51A	Midway	29 0	1 7	30 7	28 0	3 9	31 9	104
51B	Midway	29 5	1 3	30 8	29 2	3 1	32 3	105
52A	Midway	28 0	2 1	30 1	25 5	5 0	30 5	101
52B	Midway	29 2	2 9	32 1	24 5	6 7	31 2	97
Mean		28 4	2 07	30 5	25 9	4 83	30 7	100 8

IMPACT STRENGTH CORRECTED BY TOTAL LENGTH FACTORS

		$1L = 3$ Ft-lb				$1L = 7$ Ft-lb		
11	Midway	28 2	2 0	30 2	25 0	4 7	29 7	98
11	Center	27 7	2 6	30 3	22 2	6 2	28 4	94
12	Midway	28 5	1 8	30 3	26 7	4 1	30 8	102
12	Center	28 2	1 9	30 1	25 0	4 3	29 3	97
13	Midway	27 2	1 9	29 1	27 2	4 5	31 7	109
13	Center	28 0	1 7	29 7	24 2	4 0	28 2	95
21	Midway	30 0	2 1	32 1	28 5	4 8	33 3	104
21	Center	28 7	2 1	30 8	25 2	4 8	30 0	98
22	Midway	28 2	1 6	29 8	26 5	3 8	30 3	102
22	Center	29 0	1 6	30 6	24 5	3 8	28 3	93
31A	Midway	29 7	1 4	31 1	27 2	3 1	30 3	97
31B	Midway	28 7	1 1	29 8	27 0	2 6	29 6	99
41A	Midway	28 0	1 9	29 9	23 5	4 5	28 0	94
41B	Midway	26 2	2 3	28 5	27 2	5 5	32 7	115
51A	Midway	29 0	1 3	30 3	28 0	3 0	31 0	102
51B	Midway	29 5	1 4	30 9	29 2	3 1	32 3	100
52A	Midway	28 0	2 2	30 2	25.5	5 0	30 5	101
52B	Midway	29 2	2 4	31 6	24 5	5 5	30 0	95
Mean		28 4	1 85	30 3	25 9	4 29	30 2	99 7

TABLE 9 —*Corrected Impact Values, 0 15 Per Cent Carbon Nickel Steel*

ELONGATION CORRECTED BY NUMBER FACTORS

Spec-imen No	Location	Longitudinal			Transverse			Ratio Corrected Transverse / Longitudinal × 100
		Actual Elong, Per Cent	Correction Elong, Per Cent 1 n = 0 03 Per Cent	Corrected Elong, Per Cent	Actual Elong, Per Cent	Correction Elong, Per Cent 1 n = 0 07 Per Cent	Corrected Elong, Per Cent	
11	Midway	41 0	2 3	43 3	35 0	5 4	40 4	93
11	Center	40 0	2 4	42 4	33 0	5 5	38 5	91
12	Midway	41 0	2 0	43 0	36 0	4 8	40 8	95
12	Center	41 0	2 0	43 0	35 0	4 6	39 6	92
13	Midway	40 0	2 2	42 2	38 0	5 0	43 0	102
13	Center	40 0	2 2	42 2	33 0	5 0	38 0	90
21	Midway	39 0	2 4	41 4	37 2	5 7	42 9	104
21	Center	39 0	2 3	41 3	34 0	5 5	39 5	96
22	Midway	38 5	2 1	40 6	33 0	4 8	37 8	93
22	Center	39 0	2 0	41 0	32 0	4 8	36 8	90
31A	Midway	40 0	1 3	41 3	35 0	3 0	38 0	92
31B	Midway	37 0	1 3	38 3	34 0	3 0	37 0	97
41A	Midway	38 0	2 3	40 3	31 0	5 4	36 4	90
41B	Midway	32 0	2 5	34 5	34 0	5 8	39 8	115
51A	Midway	40 0	1 7	41 7	36 0	3 9	39 9	96
51B	Midway	39 0	1 3	40 3	38 0	3 1	41 1	102
52A	Midway	39 0	2 1	41 1	35 0	5 0	40 0	97
52B	Midway	40 0	2 9	42 9	33 0	6 7	39 7	93
Mean		39 1	2 07	41 1	34 6	4 83	39 9	96

ELONGATION CORRECTED BY TOTAL LENGTH FACTORS

Spec-imen No	Location	Actual Elong, Per Cent	1L = 3 Per Cent	Corrected Elong, Per Cent	Actual Elong, Per Cent	1L = 8 Per Cent	Corrected Elong, Per Cent	Ratio × 100
11	Midway	41 0	2 0	43 0	35 0	5 4	40 4	94
11	Center	40 0	2 6	42 6	33 0	7 1	40 1	94
12	Midway	41 0	1 8	42 8	36 0	4 7	40 7	95
12	Center	41 0	1 9	42 9	35 0	5 0	40 0	93
13	Midway	40 0	1 9	41 9	38 0	5 1	43 1	103
13	Center	40 0	1 7	41 7	33 0	4 6	37 6	90
21	Midway	39 0	2 1	41 1	37 2	5 5	42 7	104
21	Center	39 0	2 1	41 1	34 0	5 5	39 5	96
22	Midway	38 5	1 6	40 1	33 0	4 3	37 3	93
22	Center	39 0	1 6	40 6	32 0	4 3	36 3	89
31A	Midway	40 0	1 4	41 4	35 0	3 6	38 6	93
31B	Midway	37 0	1 1	38 1	34 0	3 0	37 0	97
41A	Midway	38 0	1 9	39 9	31 0	5 1	36 1	90
41B	Midway	32 0	2 3	34 3	34 0	6 2	40 2	117
51A	Midway	40 0	1 3	41 3	36 0	3 4	39 4	95
51B	Midway	39 0	1 4	40 4	38 0	3 6	41 6	103
52A	Midway	39 0	2 2	41 2	35 0	5 8	40 8	99
52B	Midway	40 0	2 4	42 4	33 0	6 3	39 3	93
Mean		39 1	1 85	40 9	34 6	4 91	39 5	96 4

with those of other specimens, and that the high values obtained from this heat make the computed correction lower than the apparent, true correction   This marked effect of heat 8 is illustrated best by showing the figures that result when this heat is omitted, which are given in Table 13 and Fig 14   Here the corrected values of impact strength become approximately constant with respect to inclusions at about 35 ft-lb , and
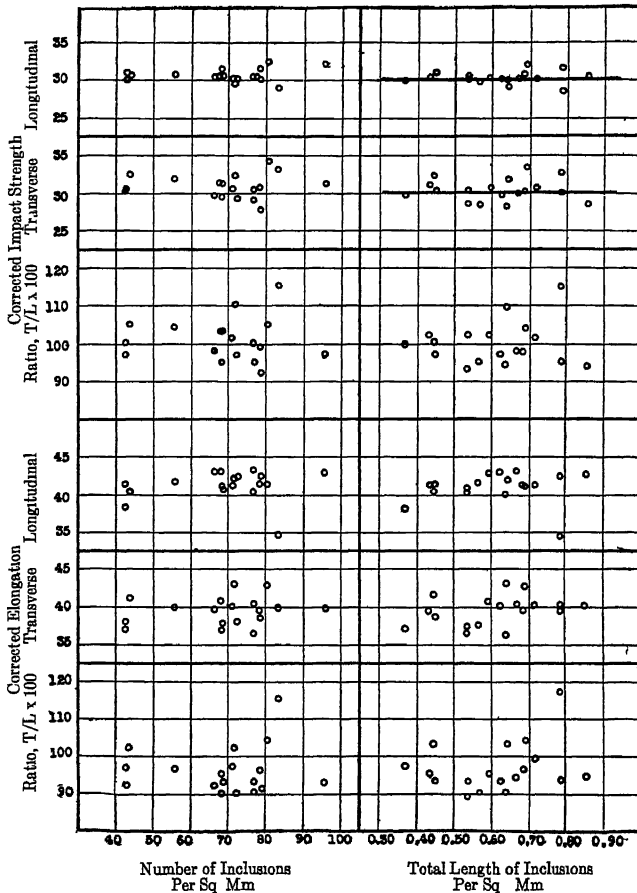
FIG 12 —CORRECTED VALUES, NICKEL STEEL, 0 15 PER CENT CARBON

the ratio between transverse and longitudinal is constant at about 100 per cent   It is believed that this represents conditions more truly than when heat 8 is included   The reasons for the exceptional values for heat 8 will be discussed later

It is evident from the curves and tables that this correlation gives a definite relation between dynamic strength and inclusions as determined here, with the exception of certain erratic values that will be con-
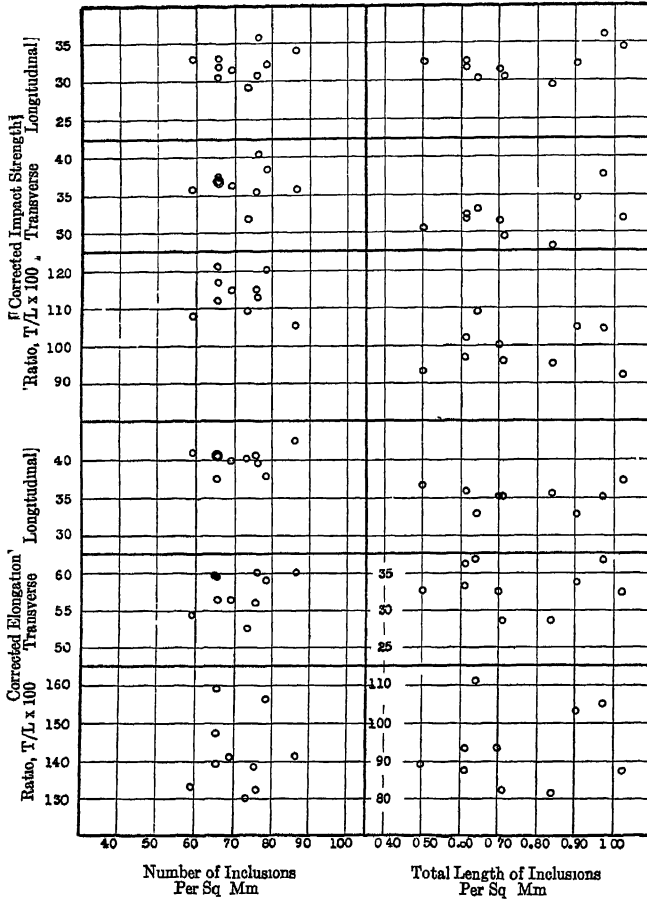
FIG 13 —CORRECTED VALUES, CHROMIUM-VANADIUM STEEL, 0 30 PER CENT CARBON

TABLE 10.—*Summary of Corrected Values, 0.30 Per Cent. Carbon Chromium-vanadium Steel*

Inclusion Summary	Direction of Tests	Impact Strength			Elongation		
		Correction Factor, Ft-lb	Mean Correct Ft-lb	Corrected Mean, Ft-lb	Correction Factor, Per Cent	Mean Correct, Per Cent	Corrected Mean, Per Cent
Number	Long	ln = 0 03	2 16	32 2	ln = 0 10	7 12	40 0
	Trans	ln = 0 20	14 24	36 5	ln = 0 50	35 6	57 4
Total length	Long	1L = 3	2 24	32 3	1L = 3	2 24	35 1
	Trans.	1L = 13	9 75	32 1	1L = 15	11 26	33 1

TABLE 11 —*Corrected Impact Values,* 0 30 *Per Cent. Carbon Chromium-vanadium Steel*

IMPACT STRENGTH CORRECTED BY NUMBER FACTORS

Specimen No	Location	Longitudinal			Transverse			Ratio Corrected Transverse / Longitudinal × 100
		Actual Imp Str, Ft-lb	Correction Imp Str , Ft-lb 1 n = 0 03 Ft-lb	Corrected Imp Str , Ft-lb	Actual Imp Str, Ft-lb	Correction Imp Str , Ft-lb 1 n = 0 20 Ft-lb	Corrected Imp Str , Ft-lb	
61	Midway	28 5	2 3	30 8	20 2	15 2	35 4	115
61	Center	29 5	2.1	31 6	22 5	13 8	36 3	115
71	Midway	31 2	1 8	33 0	24 0	11 8	35 8	108
71	Center	30 0	2 0	32 0	24 5	13 0	37 5	117
72	Midway	31 0	2 0	33 0	24 0	13 0	37 0	112
72	Center	28 5	2 0	30 5	24 7	13 0	37 7	121
81	Midway	31 5	2 6	34 1	18 5	17 2	35 7	105
81	Center	27 0	2 2	29 2	17 2	14 6	31 8	109
82	Midway	33 5	2 3	35 8	25 2	15 2	40 4	113
82	Center	29 7	2 3	32 0	22 7	15 6	38 3	120
Mean		30 0	2 16	32 2	22 3	14 2	36 5	113 5

IMPACT STRENGTH CORRECTED BY TOTAL LENGTH FACTORS

			1L = 3 Ft-lb.			1L = 13 Ft-lb		
61	Midway	28 5	2 1	30 6	20 2	9 2	29 4	96
61	Center	29 5	2 1	31 6	22 5	9 1	31 6	100
71	Midway	31 2	1 5	32 7	24 0	6 5	30 5	93
71	Center	30 0	1 8	31 8	24 5	7 9	32 4	102
72	Midway	31 0	1 8	32 8	24 0	7 9	31 9	97
72	Center	28 5	1 9	30 4	24 7	8 3	33 0	109
81	Midway	31 5	3 1	34 6	18 5	13 3	31 8	92
81	Center	27 0	2 5	29 5	17 2	10 9	28 1	95
82	Midway	33 5	2 9	36 4	25 2	12 6	37 8	104
82	Center	29 7	2 7	32 4	22 7	11 8	34 5	105
Mean		30 0	2 24	32 3	22 3	9 75	32 1	99 3

TABLE 12 —*Corrected Impact Values, 0 30 Per Cent Carbon Chromium-vanadium Steel*

ELONGATION CORRECTED BY NUMBER FACTORS

Specimen No	Location	Longitudinal			Transverse			Ratio Corrected Transverse / Longitudinal × 100
		Actual Elong, Per Cent	Correction Elong, Per Cent 1 n = 0 10 Per Cent	Corrected Elong, Per Cent	Actual Elong Per Cent	Correction Elong, Per Cent 1 n = 0 50 Per Cent	Corrected Elong, Per Cent	
61	Midway	33 0	7 6	40 6	18 0	38 0	56 0	138
61	Center	33 0	6 9	39 9	22 0	34 5	56 5	141
71	Midway	35 0	5 9	40 9	25 0	29 5	54 5	133
71	Center	34 0	6 5	40 5	27 0	32 5	59 5	147
72	Midway	34 0	6 5	40 5	24 0	32 5	56 5	139
72	Center	31 0	6 5	37 5	27 0	32 5	59 5	159
81	Midway	34 0	8 6	42 6	17 0	43 0	60 0	141
81	Center	33 0	7 3	40 3	16 0	36 5	52 5	130
82	Midway	32 0	7 6	39 6	22 0	38 0	60 0	132
82	Center	30 0	7 8	37 8	20 0	39 0	59 0	156
Mean		32 9	7 12	40 0	21 8	35 6	57 4	141 8

ELONGATION CORRECTED BY TOTAL LENGTH FACTORS

Specimen No	Location	Actual Elong	1L = 3 Per Cent	Corrected Elong	Actual Elong	1L = 15 Per Cent	Corrected Elong	Ratio
61	Midway	33 0	2 1	35 1	18 0	10 6	28 6	82
61	Center	33 0	2 1	35 1	22 0	10 5	32 5	93
71	Midway	35 0	1 5	36 5	25 0	7 5	32 5	89
71	Center	34 0	1 8	35 8	27 0	9 2	36 2	87
72	Midway	34 0	1 8	35 8	24 0	9 2	33 2	93
72	Center	31 0	1 9	32 9	27 0	9 6	36 6	111
81	Midway	34 0	3 1	37 1	17 0	15 3	32 3	87
81	Center	33 0	2 5	35 5	16 0	12 6	28 6	81
82	Midway	32 0	2 9	34 9	22 0	14 5	36 5	105
82	Center	30 0	2 7	32 7	20 0	13 6	33 6	103
Mean		32 9	2 24	35 1	21 8	11 26	33 1	92 1

TABLE 13 —*Corrected Impact Values, 0.30 Per Cent Carbon Chromium-vanadium Steel without Heat No 8*

IMPACT STRENGTH CORRECTED BY TOTAL LENGTH FACTORS

Specimen No	Location	Longitudinal			Transverse			Ratio Corrected Transverse / Longitudinal × 100
		Actual Imp Str, Ft-lb	Correction Imp Str, Ft-lb 1L = 8	Corrected Imp Str, Ft-lb	Actual Imp Str, Ft-lb	Correction Imp Str, Ft-lb 1L = 18	Corrected Imp Str, Ft-lb	
61	Midway	28 5	5 7	34 2	20 2	12 8	33 0	97
	Center	29 5	5 6	35 1	22 5	12 6	35 1	100
71	Midway	31 2	4 0	35 2	24 0	9 0	33 0	94
	Center	30 0	4 9	34 9	24 5	11 0	35 5	102
72	Midway	31 0	4 9	35 9	24 0	11 0	35 0	97
	Center	28 5	5 1	33 6	24 7	11 5	36 2	108
Mean		29 7	5 03	34 8	23 3	11 3	34 6	99 7

sidered later   Moreover, when total length per unit area rather than number per unit area is used as a measure of inclusions, variations from the mean relation are fewer, indicating that this function of the inclusions is the more pertinent factor

An attempt has been made to correct the values with respect to variations in hardness   The difference between the potential maximum of 30.5 ft-lb for 0 15 per cent. carbon nickel steel, and 35 ft-lb. for the 0 30 per cent carbon chromium-vanadium steel is believed to be due to the difference in hardness, i e, potential dynamic strength increases with hardness in this range.   However, as the hardness increases the loss of strength due to inclusions also increases.   We have, therefore, two opposing effects of hardness, and the resolution of these factors was found to be too complex to admit of solution with the

FIG 14 —CORRECTED VALUES, CHROMIUM-VANADIUM STEEL WITHOUT NICKEL, HEAT 8

data available   Although it was possible to reduce slightly the variation from the mean of the corrected values by a simple correction for hardness, this was not sufficient to affect the conclusions.   As the nature of the effect was not well understood, corrections for variation in hardness have not been included.   This limitation restricts the application of the data given here to steels of the same hardness.   Were adequate data available,

it should be expected that the hardness correction would make inclusion corrections applicable to any steel

CORRELATION OF VISIBLE INCLUSION COUNT AND COMMERCIAL RATING OF INCLUSIONS

These steels were given the customary commercial inspection for inclusions by the manufacturer, and were rated according to a scale in

Number of Inclusions
Per Sq Mm

Total Length of Inclusions
Per Sq Mm
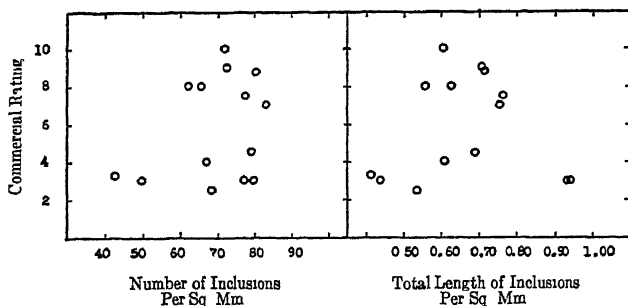
FIG 15 —RELATION BETWEEN COMMERCIAL RATING AND COUNTED INCLUSIONS

which a very clean steel is designated as "1" and a very dirty steel as "10." These figures are appended to Table 3, and their relation to the inclusion count obtained is shown in Fig 15. It is apparent that the trend is not marked, and that the variations from the trend are great   In such inspections, more weight is assigned to large inclusions, as is evidenced by the better relation with total length.

The relation of the commercial rating to impact strength (Fig. 16) is fairly good in some cases and of no value in others.   Since this method of determining inclusion content is so unreliable with respect to either inclusion count or tensile-impact results, it is evident that the pertinence of the present commercial inclusion rating should be seriously considered with respect to both cleanliness and dynamic properties.

Commercial Rating of Inclusions
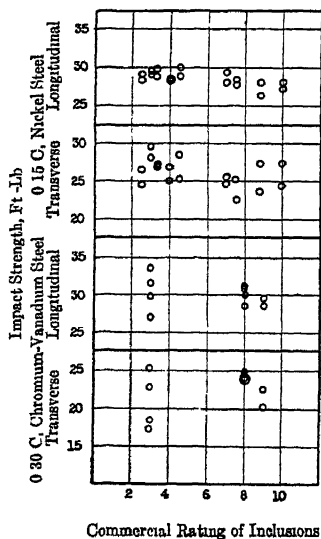
FIG 16 —RELATION OF COMMERCIAL RATING OF INCLUSIONS TO IMPACT STRENGTH.

CHEMICAL ESTIMATION OF INCLUSIONS AND OXYGEN, AND CORRELATION WITH VISIBLE INCLUSIONS AND DYNAMIC STRENGTH

Vacuum fusion analysis for oxygen, and extraction and analysis of inclusions by means of a modified iodine solution method, were also carried out on the steels studied   The former is

the usual U S. Bureau of Standards method, of which results are given in Table 14 The extraction method is an improved method developed at our laboratories It consists essentially of solution of the metallics and the sulfides in an aqueous solution of iodine and ferric iodide with ammonium citrate as an inhibitor The solution is filtered and the nonmetallic residue analyzed Any nitrides present are reported as oxides As this method has not yet been worked out for chromium-vanadium steels, the analysis was restricted to the nickel steels. The absolute accuracy of the results is not vouched for at this time, but the ability to check results and to correlate with known differences indicates that any errors are constant or proportional, and that the relative accuracy is of a high order The results of this analysis are given in Table 14. Manganese sulfide as computed from total sulfur is also listed in this table

TABLE 14.—*Chemical Determination of Inclusion Content*

| Specimen No | Oxidic Inclusions by Iodine Extraction, Per Cent | | | | | Manganese Sulfide, Per Cent | Sum Oxide Plus Sulfide, Per Cent | $\frac{\text{Oxides}}{\text{MnS}} \times 100$ | Vacuum Fusion Oxygen, Per Cent | Inclusion Content | |
	FeO	MnO	SiO₂	Al₂O₃	Total					Number per Sq Mm	Total Length per Sq Mm
11	0 022	0 006	0 008	Nil	0 038	0 054	0 092	70	0 009	77 8	0 761
12	0 027	0 006	0 006	Nil	0 041	0 049	0 090	84	0 009	67 0	0 608
13	0 030	0 008	0 008	Nil	0 050	0 054	0 104	93	0 009	72 0	0 603
21	0 033	0 007	0 002	Nil	0 044	0 057	0 101	77	0 009	79 5	0 688
22	0 025	0 006	0 008	Nil	0 045	0 062	0 107	73	0 013	68 3	0 536
31A	0 022	0 010	0 006	Nil	0 038	0 087	0 125	44	0 008	42 8	0 450
31B	0 022	0 010	0 006	Nil	0 038	0 103	0 141	37	0 008	42 8	0 370
41A	0 022	0 010	0 005	Nil	0 043	0 049	0 092	88	0 007	76 9	0 638
41B	0 013	0 005	0 007	Nil	0 027	0 060	0 087	45	0 008	83 4	0 784
51A	0 030	0 007	0 005	Nil	0 042	0 081	0 123	52	0 007	55 8	0 432
51B	0 025	0 008	0 006	Nil	0 039	0 068	0 107	57	0 007	43 7	0 446
52A	0 043	0 010	0 011	Nil	0 064	0 057	0 121	112	0 008	71 1	0 716
52B	0 039	0 009	0 011	Nil	0 061	0 049	0 110	124	0 009	95 6	0 786
61									0 005	72 3	0 707
71									0 007	62 2	0 557
72									0 004	65 3	0 625
81									0 004	79.7	0 931
82									0 006	77 1	0 939

All attempts to correlate vacuum fusion oxygen with the visible inclusions, the dynamic strength, the commercial rating, or any function involving these, failed This lack of relation between vacuum fusion oxygen and other characteristics of steels is notable, but is in line with our previous experience. This serves to emphasize the importance of the physical as well as the chemical nature of foreign matter in steels

A graphic study of the relation of extracted inclusions to inclusion count and dynamic properties shows distinct trends, particularly when sulfides are also considered. The curves (Fig 17) establish a trend in which the visible inclusions increase with the extracted inclusions Furthermore, a trend is shown in which the visible inclusions decrease with increase of the sulfides and with the sum of the sulfides plus oxides, and a similar trend exists in their relation to dynamic strength (Fig 18). However, the true significance of these trends is evident only when the interrelation of the oxides and sulfides is considered This is done in Fig. 19, in which the ratio of extracted inclusions to sulfides is shown in relation to the total length of inclusions per unit area. The points on this curve are so remarkably in line as to establish a quantitative relation, and the exceptions are of such a nature as to indicate the existence of another causal factor. Moreover, this curve shows that, in general, there is a constant relation between the counted inclusions and all inclusions large enough to be retained on filter paper. The minimum size of the counted inclusions is 0 005 mm., whereas of those retained on the filter paper the mean minimum value is probably of the order of 0 001 mm Further, the isolated points having a marked deviation from the mean show that in certain cases the above-mentioned constant relation may be changed by an appreciable amount.

FIG 17 —RELATION OF OXIDE INCLUSIONS, MANGANESE SULFIDE AND THEIR SUM TO TOTAL LENGTH OF INCLUSIONS

It is significant that in two of the three bars representing the isolated points, the correlation between dynamic strength and total length of inclusions gives a deviation from the mean, the extent of which is greater than with any of the other bars Moreover, the impact strength of the exceptional bars is in some cases better and in some worse than would be indicated by the inclusion figures. The correlation of the oxide-sulfide ratio with counted inclusions does not hold when the specific constituents rather than total inclusions are considered This indicates a physical and not a chemical factor,

and shows that within the limits of this study the composition of the inclusions has no effect on the physical properties of the steel, except as it affects the number and size of inclusions
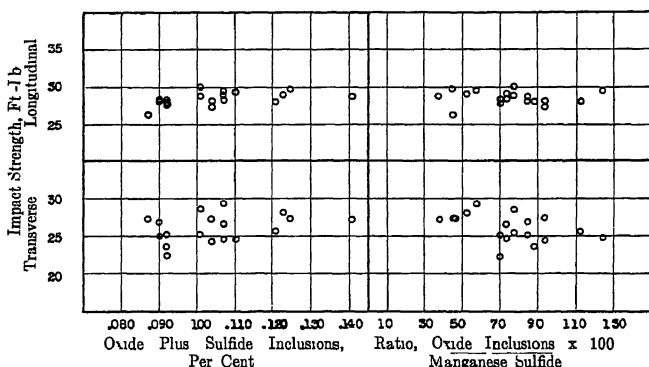
FIG 18 —EXPERIMENTAL VALUES, NICKEL STEEL, 0 15 PER CENT CARBON

Here we have a promising clue to the matter of body in steel   "Body" is a term long used by steelmakers   We choose to designate it as that characteristic of a steel which enables it to have more resistance to dynamic stresses than would be expected from the physical properties on static test or from the apparent cleanliness or lack of cleanliness of the steel   From this study it would certainly appear to be related to the amount and distribution of nonmetallics whose size is comprised between the smallest imaginable particle and something just larger than the mean minimum particle size retained on filter paper.   An attempt to correlate these particles with the vacuum fusion oxygen has been fruitless   This whole matter is well illustrated by the steels showing the greatest deviations in this study

FIG 19 —RATIO OF OXIDE INCLUSIONS TO MANGANESE SULFIDE VERSUS TOTAL LENGTH OF INCLUSIONS

The deviations from the correlation curves are exceptional in three specific instances, namely, heats 8 and 41 and bar 21   In heat 8, the distribution of the inclusions was so erratic that no good correlation could have been hoped for. It is significant that check values within the limits of accuracy were not obtained on duplicate tensile-impact tests   This means that this heat would at once have been marked as exceptional had the dynamic test been carried out. However, according to the inclusion rating

of 3, normally it would have been put into service without question. Heat 41 presents a similar condition, but the variation in the tensile-impact values is such that the lack of correlation cannot be accounted for wholly by the distribution of the inclusions   In one part of the bar the impact values were higher than would be expected from the study of the inclusions, and in another part they were lower   We believe that this is in part due to variation in body of the steel.   Still another condition exists in the case of bar 21   The tensile-impact test consistently gives values higher than would be expected from the inclusion count, which indicates that the body of this steel is exceptionally good, and that it might well be given a much higher rating in quality than would be indicated by the inclusions

The deviations of bars 41B and 21 from the mean in the correlation curves are present not only in the inclusion length and number relation to dynamic strength, but also in their inclusion analysis and sulfide relation.   These deviations are so much greater than the mean deviations of the rest of the steels that there must be a causal factor present   Moreover, this causal factor must be associated with the oxides, nitrides and sulfides.   From the vacuum fusion oxygen and total sulfur, it is evident that the deviations are not a function of the total amounts of these elements present   Thus, they must be related to the physical state and distribution of the nonmetallics.   In the inclusion count, all inclusions less than 0 005 mm have not been counted.   In the inclusion extraction, all the inclusions whose size was less than that necessary to be retained on Whatman's No 42 filter paper (approximately 0 001 mm.) have not been measured   From the fact that the deviations appeared in both the inclusion-dynamic relation and the visible and extracted inclusion relation, it is evident that the causal factor comprises oxides and nitrides which are both larger and smaller than the smallest particle collected on the filter paper.   Based on the foregoing reasoning, it is believed that the proportion of such inclusions to the extracted and visible inclusions is an important causal factor in determining body.   It is appreciated that this statement is based on limited data, and that much more work would be necessary to substantiate this conclusion

General Discussion and Summary

The writers are aware that this study has been carried out on a limited number of heats from one source, and that this necessarily tends to put certain limits on any conclusions that may be drawn. However, the use of a single source had the very great advantage that there would be less tendency to mask such trends as might exist and would thus make the limited number more effective.   Moreover, the variation in chemical analysis of the steels, particularly with respect to manganese, sulfur, silicon and phosphorus, is such as to cover the normal variation to be expected in quality steels, particularly under S. A. E.

specifications.   It should be particularly emphasized that throughout this correlation work the actual effects may be due in part or entirely to nonvisible inclusions, solid solution material, microsegregation or other factors which are intimately associated with the visible inclusions in such a way that the inclusion count is a measure of both the visible inclusions and these other factors

The accuracy of the methods used has been established in dealing with them in this paper, but this accuracy is even more emphasized by the correlations   Any inaccuracies or errors in the methods, as far as relative values are concerned, would have been sharply emphasized in the correlation curves.   Thus these methods stand not only on their own merit but also in the way in which they check each other; i e , suitable, interrelated functions of visible inclusions, extracted inclusions, sulfides and dynamic properties all result in straight lines with the points showing a low mean deviation.

The measure of the inclusions that has been emphasized in this paper is the total length per square millimeter, although the number per square millimeter has also been used   Similarly, foot-pounds have been used as a measure of the impact strength more often than elongation.   The correlation of these units of measure with the other properties determined shows that total length and foot-pounds are the more reliable units. Within the limits of variation in the steel used, the distribution of the total length of inclusions apparently is not an important factor.   The method of correcting the impact values for inclusion content so as to give the impact strength that would have resulted had the inclusions been absent has led to very consistent results.   The longitudinal and transverse values so obtained are identical, indicating that within the limits of the steels studied there is no other factor, such as fiber, grain size or orientation, that affects the relative dynamic strengths, except as such an effect is directly proportional to the inclusion content. . The steels studied were in all cases finely pearlitic, so that we have no information on the related effect of the inclusions and the type of structure.   However, the fact that the steels are different in hardness, and that the effect of the inclusions increases with the hardness, indicates that a similar effect might be caused by structure   The importance of hardness is clearly shown, the indications being that within the limits studied the harder the steel the higher the impact value when inclusions are absent, but the greater the tendency of any given inclusion condition to lower this impact value.   As yet, sufficient data are not available to show an accurate quantitative relation between hardness and the effect of inclusions. Work on this is under way, and it is hoped that such a relation will be forthcoming

The importance of sulfur in the steels is marked, and it is shown that a quantitative relation exists between the extracted inclusions, the sulfur

content, the total length of visible inclusions and the dynamic strength The higher the sulfur for a given extracted inclusion content, the lower the visible inclusions and the greater the impact strength It is possible that had steels with higher sulfur been studied, a countertendency would have been evident Thus, sulfides must have an important bearing on the dynamic strength, and any study of the effect of oxidic inclusions on the dynamic strength must include a consideration of the sulfides It is apparent that much more work along these lines is needed, and that the importance of such work cannot be overemphasized

Factors other than inclusions are believed to be one of the most important subjects considered in this study The effect of these factors is at least of the same order of magnitude as the effect of the inclusions in the dirtiest steel. These factors have been comprised in the term "body" and the study indicates that the state of division of the inclusions which are less than 0 005 mm has a bearing on the quality of the steel It is probable that many of these inclusions are much smaller than the maximum mentioned, and may even approach molecular dimensions, and some of these nonmetallics may be present in solid solution That body was evidenced in the steels is most significant, and leads us to expect that the body would be a most important factor were steels from different sources or different processes considered

The study sheds considerable light on the present commercial method of rating steels for inclusions It shows that while this method is satisfactory in many cases it is not reliable The number of instances in which it gives no indication of the actual status of the inclusions or dynamic strength appears to be sufficiently great so that its use as the sole criterion for the cleanliness or dynamic strength of steels must be questioned. The method shown here of counting inclusions undoubtedly would give an accurate criterion of the cleanliness of the steels, but the labor involved tends to exclude it from the category of routine tests Approximately one hour per sample would be necessary Moreover, the main reason for wishing to have information about the cleanliness of the steel is essentially to know the effect of such cleanliness on the dynamic strength. In view of the fact that there are appreciable exceptions to the correlation of cleanliness and dynamic strength, it would seem that the best method of insuring satisfactory dynamic strength is the simple tensile-impact test With this test, dirty steels with normal body and clean steels with poor body could be classified as unsatisfactory. On the other hand, clean steels with normal body and relatively dirty steels with exceptionally good body could be classified as satisfactory. The tensile-impact specimen requires a small amount of machine-shop labor, and can be tested in a few minutes. The added information that would be gained from such a test would seem to warrant its use, either as an adjunct to the present inclusion rating or as a substitute for it. The

matter of preparing a satisfactory specification for dynamic test is one that could be considered only after a great many more tensile-impact tests have been performed   Simplification in the application of this test could be achieved by calibrating hardness over a narrow range, such as 80 to 90 Rockwell B, and normalizing bars so that the hardness will fall in this range.

Conclusions

The following conclusions are based on the steels here studied, so that while some are no doubt subject to modification, others by their very nature are sufficiently well established to apply generally

1 The dynamic strength of steels is quantitatively reduced by visible inclusions or factors directly proportional to them

2 The magnitude of the effect of inclusions on the dynamic strength increases with the hardness of the steel

3 Factors other than visible inclusions have an important influence on the dynamic strength of steels, and are comprised in the term "body."

4 Body is markedly influenced by minute inclusions whose size is less than 0 005 millimeter

5. Visible inclusions are directly proportional to the ratio of extracted inclusions to sulfides in the steels studied

6. The "total length" of inclusions per square millimeter is a satisfactory measure of the cleanliness of steels

7 The tensile-impact test is a satisfactory measure of the dynamic quality of steels

8 The present commercial inclusion rating is not a reliable measure of the cleanliness or dynamic strength of steels, although it does give satisfactory indications in many instances   .

DISCUSSION

(G B Waterhouse presiding)

R. S Dean, Washington, D. C (written discussion*) —While one may conclude from purely common-sense reasoning that inclusions are undesirable in steel, the data of the present paper seem to me to be in agreement with other data on the subject in establishing that the quantitative relation which exists between visible inclusions and physical properties in commercial steel is almost if not completely masked by other factors.

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Whether these other factors are the inclusions of sizes not within the arbitrarily selected range or are unrelated factors cannot be determined. Sufficient data would now seem to be at hand, however, to indicate that physical properties are not likely to be correlated with any arbitrarily selected size range of inclusions, and the next step would seem to be to determine the size distribution of inclusions in the steel under investigation. It is probable that the distribution of particle size of inclusions is Maxwellian, as it is in emulsions, and Fig 5, therefore, is interesting in indicating that the inclusions dealt with in this paper are entirely on one side of the distribution maximum. A range symmetrical with this maximum certainly would have been a more logical selection.

It is not by any means a foregone conclusion, however, that the effect of other than very large inclusions on physical properties may not in most cases be masked by unavoidable variations in composition and treatment, and a little care may be necessary lest the steel metallurgists of 1931 be at some future time likened to ostriches with their heads buried in the solid nonmetallic inclusions.

H Styri, Philadelphia, Pa (written discussion) —In connection with the results obtained by Kinzel and Crafts in their elaborate and careful study of the effect of slag inclusions on the dynamic strength of steel it may be worth while to recall a somewhat similar comparative study between the slag inclusions and physical properties of steel which was published as a paper in *Chemical and Metallurgical Engineering*, April, 1919. In name the investigation was a study on flakes in steel but developed into a study of slags. A great number of fractures of transverse tensile test pieces from gun forgings were examined in the binocular microscope with a magnification of about 80. The number and appearance of the slag inclusions were noted for each fracture and arranged in a table in descending order. Afterwards corresponding physical properties—tensile strength, elastic limit, elongation and contraction—were added. It was found that there was a close general connection between the number of slag inclusions and the elongation and contraction. For large amounts the elongation, and particularly the contraction, was small. The elastic limit and tensile strength, however, were not so much affected. The examination was carefully made and, quoting from the paper, "the first approximately quantitative proof can be given of the influence of slag inclusion on physical properties of steels with practically the same heat treatment, particularly on elongation and contraction. It is most striking to find that in all good test bars examined, either no slag particles or only very small round particles or traces of them are found."

In addition to the transverse bars, a number of longitudinal bars were examined and similar relations were found, although less pronounced.

When we consider that the energy consumed in pulling a tensile test piece can be evaluated approximately by the product of elongation and tensile strength, the conclusion is parallel with the one given in the paper that the dynamic strength is quantitatively reduced by visible inclusions.

I. N Goff, W G Crane and H J Dillon, Indiana Harbor, Ind (written discussion) —A critical discussion of the methods employed by the authors in their work will not be attempted, as it is realized that unusual precautions were taken to avoid the effects of segregation, nonuniformity in hardness and other factors that would affect the results. However, questions will be brought up concerning polishing and etching technique used.

Table 2 shows clearly that in practically every case the impact strength of transverse test pieces is much lower than that of the longitudinal pieces. It is brought out in the paper that this difference is due to the visible inclusions or factors varying directly with these inclusions. Since the comparison in each case was made between transverse and longitudinal tests cut from the same bar, it is obvious that the actual

inclusion content would be practically the same The quantity of inclusions in a given pair of tests, therefore, could not explain the difference in impact values The authors modified their statement by saying that the difference could be explained by the inclusions "or factors varying directly with these inclusions" We believe the latter part of this statement to be the essential matter to be considered What are the factors varying with the inclusions that are different in the two cases? One fact that is known is that the orientations of the inclusions differ

When a bar of steel is rolled, the foreign material composing the inclusions is more or less plastic at the temperature of rolling and will be elongated in the direction of rolling A considerable quantity of these nonmetallics will assume the shape of elongated threadlike fibers running longitudinally with the bar Greater resistance to tensile impact would accordingly be shown longitudinally rather than in a transverse direction, since the stresses in the longitudinal piece would be largely on strands of solid metal unbroken by crosspieces of foreign matter

In using an inclusion count in this connection it has occurred to the writers that the probabilities of error are greater in examining longitudinal specimens than in those taken transversely In transverse specimens the retention of these fibers is not difficult, since we cut and polish at right angles to their length and they are embedded firmly enough to prevent wiping or gouging out In the longitudinal direction we cut and polish parallel to the length of the inclusion According to the work of various investigators, the bond that exists between the various types of inclusions and the metal proper is very weak Hence if we cut or polish to a point where the metal no longer locks the inclusion in, it is wiped out, and on continued polishing the existing cavity is greatly accentuated This is, of course, a source of error, and the authors have probably reduced it to a minimum after experimenting with various types of polishing media.

The question also arises, in discussing polishing and etching, whether undue emphasis might not have been placed on sulfide inclusions by the use of 10 per cent chromic acid solution Would they appear any more noticeable in counting than the oxidic inclusions? On the contrary, however, it was observed in Table 3 that the steels with the highest sulfur content showed the lowest inclusion count This fact, along with a fairly uniform oxidic inclusion content, accounts for the straight-line graph obtained in Fig. 19

In Table 14, the determination of inclusion content by the iodine extraction method especially interested us The oxide inclusions FeO, MnO and SiO_2 compare closely to results we have obtained by the chlorine extraction method The Al_2O_3 content was lower than ours

This paper is of especial interest to both the manufacturer and user of rail steel The trend today is toward the production of a harder rail with a consequent increase in wearing qualities The authors make note of the effect of inclusions on hard steels when they state that within the limits studied the harder the steel, the higher the impact value when inclusions are absent, but that a given amount of inclusions produces a more detrimental effect on the harder steels

It will be well to keep this statement in mind in work directed toward rails of increased hardness In other words, whether we increase the hardness of a steel by quenching or by an alloy addition, the condition or state of cleanliness is still one of the prime factors

The authors' point relative to the present commercial method of rating steels for inclusions is well taken. It cannot honestly be said that present methods approach any degree of accuracy Manufacturing on a production basis often places the metallographist's tests on the same basis and such work cannot be done properly in the time allotted to it Hence the inclusion rating becomes meaningless To do this work on successive stages of dry paper, finishing with one final wet lapping

operation, is, as the authors point out, arduous and not conducive to rapid deter-minations   A method whereby an accurate, rapid test may be made will be a welcome innovation

In discussing physical testing of steel specimens, the question comes up as to what relation, if any, exists between tensile impact and fatigue strength?   Would a dirty steel with an exceptionally good body, which would be classed as good according to the tensile impact test, receive the same classification after fatigue testing?

The authors have shown, by applying mathematical corrections to experimentally determined impact values, that if the inclusions were absent the steels would have the same strength either longitudinally or transversely   They say (p 171) that they do not believe that factors "such as fiber, grain size or orientation affect the relative dynamic strength except as such an effect is directly proportional to the inclusion content "   Since the bars were all normalized before testing, the grain structure was supposed to have been made uniform in each direction, but normalizing would not change the orientation of the inclusions   We believe that this factor of orientation largely accounts for the observed differences in strength   Present methods of steel manufacture requiring rolling will always give this effect of inclusion orientation, and there is no way of avoiding this   Hence, work must still be directed toward eliminating or reducing the number of inclusions and producing cleaner steel

H W GRAHAM, Pittsburgh, Pa (written discussion) —By such reading and study as we have been able to give the preprint of this paper, we have not found it convinc-ing   It would appear that the authors are dealing with the equation that dynamic strength is proportional to the influence of inclusions and of a vague physical entity which they propose to call "body"   This mathematical equation contains two unknown quantities   The authors appear to conclude that no evaluation of the effect of "body" is possible, nevertheless they proceed to attempt to evaluate the influences of inclusions   Such a procedure hardly appears to be sound mathematics

We do not attempt to propose any dogmatic objection to the theory that physical properties are influenced by inclusions, but the experiences of a number of years of intensive study of all recognizable influences upon the behavior of steel in manufacture, in fabrication, and in service have left us with the feeling that inclusions are not by any means the largest influence   Perhaps if confined within the limits of a small lot of steel, perhaps even up to the extent of an entire heat of steel, except as influenced by segregation (chemical or otherwise), inclusions may possibly be the chief governing influence upon physical properties, but in comparing the different heats of steel in the same grade, and particularly different grades of steel, one rapidly loses grasp of any basis of correlation between physical properties and inclusions

The authors state that all samples have been normalized "to obtain uniformity " We wonder what uniformity of grain size was found to exist?   It has been our experi-ence that each heat of steel has its own characteristics of grain size and that uniform thermal treatment in normalizing does not necessarily achieve uniformity of grain size   In fact, in the paper under discussion the tension impact results show a varia-tion that is about what we would expect from variation in grain size, irrespective of inclusions

The investigators evidently have explored impact in bending and discarded this test for impact in tension   Our own experience tends rather to a reverse conclusion, since we have become convinced that the better check results obtained in tension impact are simply due to the fact that this test is a relatively insensitive one

Considering the subject in general, it is difficult to argue convincingly that inclu-sions are a proportionately large influence in the varying behavior of steel products under the various conditions of fabrication and service   The variation in hardness and physical properties under various heat-treating operations, the always varying and somewhat erratic behavior of steel under conditions of machining, the variation

in welding results from one lot of steel to another, the differences found in cold-forming operations such as are practiced on automobile sheets—these and a host of other observed phenomena offer no consistent correlation with the total amount of inclusions or any subclassification thereof

When confined to the single condition of impact strength as considered by Mr Kinzel and Mr Crafts, one is inclined to suspect that inclusions are a proportionately less important fact than what the authors have called "body" It is our conviction that inclusions are the one-seventh of the iceberg that projects above the surface of the ocean, and that "body," or some such vague aggregate of influences, constitutes the other six-sevenths of the iceberg volume We further believe that this metaphor is apt, in that it is on the portion of the iceberg which is below the surface of the ocean that the ship strikes, and it is this portion which does the damage and not the one-seventh that can be seen

In other words, we are convinced that inclusions visible under the microscope are not nearly so harmful as the conditions that are submicroscopic There is much reason to suspect the existence of colloidal or emulsified materials existing in pseudo or actual solid solution, which vigorously affect the quality and behavior of steel We understand that Mr Kinzel intends to carry on further research directed toward a knowledge of these vague and almost unknown influences, and along this path we wish Mr Kinzel and his associate good luck and rapid progress

C H HERTY, JR, Pittsburgh, Pa (written discussion*) —There has been so much controversy regarding the effect of inclusions, and so much speculation, that definite data such as are included in this paper are important

In general, we believe that the results of studies of the impact tensiles versus the inclusion count are trustworthy, but we consider it somewhat unfortunate that the authors attempted with the data at hand to go further into the question of correction of impact tensiles for inclusions The method of correction shown in Fig 8 is logical, but the results shown in Figs 9a and 9b are disappointing and would tend to show that other factors which the authors include in the term "body" are important—fully as important as they claim The authors would have made a stronger argument for their data had they shown the method of correction and not attempted to apply the present results until more could have been added Some of the lines drawn in Fig 9b are mystifying, and apparently could have been drawn with other slopes which would have fitted the points better Other individual plots in these two figures would require many more data to enable one to draw any line through the plots In connection with Fig 5, had the authors enlarged their scale of impact values, the trend for decreasing impact with increasing inclusion content would have been much more pronounced to the eye

There might be considerable argument regarding the method of determining the inclusion content by the count method used by the authors For example, which would be the more detrimental, an inclusion 10 microns in length and 1 micron in diameter, or one 10 microns in length and 6 microns in diameter? From consideration of stresses at the ends of the inclusions, one would believe that the second type of inclusion would be much more harmful than the first, but the authors have not made any mention of the size, other than the length, of the various inclusions

In the discussion of the method of differentiating between sulfide and oxide inclusions, the statement is made that "all specimens were etched with 10 per cent aqueous chromic-acid solution to darken the sulfides and make them more readily visible, as this etch does not attack the metal or any inclusions other than sulfides " Here apparently lies a serious error in the interpretation of the results and probably some error in the method of counting It is well known that manganese silicates will

dissolve manganese sulfide   We have frequently observed that a sulfur test will be obtained from a given inclusion which, upon extraction, will analyze high in silica and manganous oxide and with possibly only 5 per cent of sulfur   An example which comes to my mind is furnished by a steelmaker who sent us some broken tensile tests that showed plates of a yellowish inclusion at the break   He contended that these were sulfide inclusions, and it was difficult to see how he could avoid this difficulty because his steels contained only 0 018 and 0 020 per cent sulfur   When extracted, these inclusions were found to be composed almost entirely of manganese silicate with a small amount of sulfide dissolved in silicate mass   Of course the sulfide content of these inclusions gives a sulfur test with chromic acid, so that the inclusions would appear from the chromic-acid test to be sulfide, whereas they were actually manganese silicates containing some manganese sulfide   Just how far this would affect the results of this present paper cannot be judged unless the original segregation of sulfide and oxide particles is known

It is interesting to note that of the heats studied four were classed as clean and six as dirty   It is almost inconceivable that such a change in classification could have been observed in silicon-killed steel with sulfur as low as it is in these steels if the iodine-extraction results are correct   With the low sulfur shown in these steels it is almost inevitable that the variation in cleanliness was due to silicate inclusions and that the iodine results are erroneous   This matter is taken up in detail in a discussion (p 216) by G R Fitterer, of the U S Bureau of Mines, and will not be reviewed here further

We would appreciate the opportunity to make extraction of inclusions by other methods, particularly the electrolytic method, on some of the steels which gave the most marked difference in impact tests as indicated in this paper

A B KINZEL AND W CRAFTS (written discussion) —The authors wish to express their appreciation of the interest shown and the constructive nature of the discussions   Mr Dean believes that one might conclude from purely common-sense reasoning that inclusions are undesirable in steel   Even this is highly problematical, and it may well be that inclusions of a size much smaller than that with which we are here dealing are highly beneficial   They may even be the cause of the straight-line stress-strain relation which we find so desirable in ferrous alloys and which are in general lacking in the nonferrous metals   That inclusions greater than 0 005 mm are probably undesirable has been demonstrated in the paper   The purpose of this study has been to so isolate the effects due to counted inclusions that they may be considered separate from the effects of other known and unknown factors, and not be masked by these factors   The corrected curves in Figs 12 and 14 show that we have been reasonably successful in this attempt   The presence of other factors is recognized, however, and further work is under way to determine the relative importance of these other factors with respect to the inclusions   The other factors involved are grouped in the term "body," and such things as variations in composition and treatment, as mentioned by Mr Dean, are not included in this term, having been controlled in this study   Mr. Dean's observations with respect to the Maxwellian distribution of inclusions are interesting, but even a superficial study of inclusion distribution at high magnifications shows that up to the limits possible (0 0002 mm) the number of inclusions increases rapidly and logarithmically   Even from theoretical considerations, the precipitation of inclusions is different from the coagulation of particles in an emulsion, and we should expect the number of inclusions to rise rapidly until the inclusion ceases to be an inclusion and is a molecule   The method of evaluating the inclusion content, therefore, is representative in that it covers a certain bracket on a curve which varies uniformly.

It is most gratifying to receive Dr. Styri's discussion and, while his work did not deal specifically with the dynamic properties in which we are most interested, it has

in general checked the results which we report   It further emphasizes that the effect of the inclusions is made evident and can be quantitatively established when factors other than inclusions are controlled   It is particularly striking that, although we measured inclusions of a much smaller order of magnitude than those measured by Dr Styri, and included these in our inclusion index, the results are in general the same, confirming that, in general, there is a causal connection between the number of larger and smaller inclusions

The remarks of Messrs Goff, Crane and Dillon are very much to the point   In fact, to those workers in the field who have given this matter serious attention, they are also axiomatic, and we are pleased that they are emphasized at this time Transverse tensile impact strength is lower than longitudinal impact strength because of the fibrous character of the inclusions   The discussers bring this out so well that it needs no amplification   It should be pointed out that all inclusion counts were made on specimens polished parallel to the direction of rolling   Thus we avoided the errors which the discussers point out are very likely to occur on counting inclusions on sections at right angles to their length   The use of 10 per cent chromic acid for darkening sulfides has been very helpful, and anyone working with this method will realize that while the sulfides are more easily counted in this way, there is no over-emphasis involved   We are pleased to hear that our iodine extraction results are in line with the results obtained by Dr Goff and his associates with the chlorine extraction methods   As we did not work on the same steels, this is really no criterion of either method, and the difference in alumina content is understandable   In applying our results to rail steel, Dr Goff has gone beyond the limits of hardness studied   In view of the increasing importance of other factors, such as internal strain, notch propagation, etc , we do not believe that this extrapolation is justified   We are glad to have Dr Goff's associates emphasize our point of view to the effect that the present method of commercial inclusion rating is highly unsatisfactory and that any accurate method would be most arduous   Work is under way at present to correlate the properties measured by tensile-impact and fatigue tests, and will be reported later.

Mr Graham's discussion strikes at the very heart of the matter of inclusions in steel   He seems to have taken the fact that this paper deals with inclusions as an indication that we believe inclusions to be an all-important factor in the determination of physical properties   Such is not at all the case.   We have found this opinion among many metallurgists, and the purpose of this paper was to study the effect of inclusions alone to see whether or not there was any justification for the opinion that inclusions were such an all-important factor   We have chosen the transverse tensile-impact test as a measure of the dynamic properties   The figure resulting from this test is determined by hardness and other static properties, which were controlled and modified by inclusion content and by the many factors grouped in the term "body "   The steels were so chosen as to show a minimum variation in body, and we believe that we have isolated the inclusion factor and shown that increased inclusion content adversely affects the dynamic strength   We have refrained from commenting on whether the magnitude of this effect in the long run of commercial steels is of major or minor order   We merely state that, other things being equal, the inclusions do act deleteriously on the dynamic strength   It would appear, however, that the effect of inclusions in this hardness range has been greatly overestimated   It may well be that the importance of the inclusions is analogous to the visible portion of an iceberg, but as in an iceberg, there may well be some direct relation between the visible and invisible portions, and we have been careful to use the phrase "visible inclusions or factors varying directly as do these visible inclusions "   We propose to continue our studies to determine the importance of the inclusion factor itself   In doing so we are fully aware of the many apparent anomalies arising in practice, such as extra clean steels with very poor dynamic properties, and extra poor steels with extremely

good dynamic properties   The anomaly is due to what we call body, and if there is any relation between the inclusion content and the body of the steel, it may well be expected that, in a great many samples, few will show other than average body, so that the inclusion factor may well be an important indication   On the other hand, if steels are made with controlled body, either good or bad, inclusions may be of secondary importance   These are questions which we are not prepared to answer at the present time   Mr Graham's experience indicates that the answer will show the unimportance of the inclusions   Even though this may be true, we still feel that it has been well worth while to study the inclusion effect as an isolated phenomenon before attacking the more complex study of "body "

We are particularly interested to receive Dr Herty's discussion in view of his active work in this field   We are pleased to see that he considers the method used logical, but cannot agree with him that the results shown in Figs 9a and 9b are disappointing   It should be stated again that these curves were not used in the final correction due to insufficient number of points, but were merely included to illustrate the method   Fig 6 could have been made more spectacular by using different ordinates, but in view of the fact that the straight-line relation is emphatically brought out in Fig 12 using corrected values, we felt there was no need for emphasizing Fig 6   In view of the fact that all of the steels in question had approximately the same amount of reduction of area in rolling, a length measurement automatically implies a width measurement, so that length could be used as a single index for cleanliness   Thus the factor of width and length of specimen was controlled and not studied   Regarding the chromic acid etch for sulfides, it is obvious that sulfides and silicates are mutually soluble to some degree and that it is perfectly possible to have a silicon steel in which all of the inclusions would appear to be what in the past has been known as sulfides   The etching was merely to make these pale gray sulfides or sulfidesilicates more readily visible, and no attempt was made in counting to differentiate between the various types of inclusions   The remarks regarding the mutual solubility of sulfides and silicates are sufficient to explain the inclusion classification of the heats, even though they are silicon-killed and are low in sulfur, therefore no apologies for the iodine extraction method are necessary

In conclusion, the authors like to emphasize again the fact that they hold no brief for the relative importance of the inclusions in steel; that they believe that the transverse tensile impact test measures both the effect of the inclusions and the effect of other factors, and that any inclusion count which might be considered satisfactory would be entirely too arduous for commercial application   The oxide-sulfide relation shown in Fig 19 has not been particularly stressed in this discussion, and we should like to emphasize its significance   Due to the mutual solubility of sulfide and silicates, sulfur has a very important effect on the number of inclusions present, and within limits, other things being equal, the higher the sulfur, the cleaner the steel   At this time, when readily fluxing inclusions are a main topic of discussion, the role of sulfur in the formation of such inclusions should be given serious consideration

The discussion has served to emphasize the lack of knowledge with respect to inclusions and body of steel   It has brought out many points of view, all of which may well be reconciled by a general increase of knowledge pertaining to the problem   As the points of view differ in degree rather than in kind, this emphasizes the need for quantitative work   The problem is so vast that it cannot be attacked as a whole   Segregation into individual factors seems to be the most logical way to acquire the much needed information and it was with full realization of the scope of the problem that the most readily studied of the inclusion factors was attacked   We expect to continue working on the problem as a whole and trust that other workers too will turn their attention to quantitative studies, so that in the not too distant future our understanding will be clearer.

Inclusions and Their Effect on Impact Strength of Steel, II*

By A. B. Kinzel† and Walter Crafts,† New York, N. Y.

A PREVIOUS study[1] of the relations of impact strength to inclusions showed that the dynamic strength of steel is lowered by the presence of visible counted inclusions, but that other factors comprised in the term "body" have a marked influence   The previous work was carried out on selected steels from a single source, so that the body factor was purposely minimized, but even under these conditions it was found that inclusion counting or the use of the commercial inclusion rating is not satisfactory The tensile-impact test, however, was indicated as a satisfactory measure of dynamic strength.   It was further suggested that the tensile-impact test should be so standardized as to be suitable for use in specifications, and that the hardness factor should be worked out over a sufficient range to admit ready commercial use of the tensile-impact test

In accordance with these suggestions, and in view of the fact that the steels reported in the previous paper were selected and treated so as to have a minimum variation in body, hardness and structure, further work has been performed on a variety of steels which are not limited by these conditions   The word "body" is used here for want of a better term   It is simply a convenient expression which comprises the effect of the various unknown factors that modify the dynamic strength of the steel   Thus at our present state of knowledge, the writers have chosen to consider hardness, structure and counted inclusion content as factors not comprised in the term "body," and such factors as raw materials, process of melting, fabricating, etc , as comprised in the term "body "

Numerous grades of steels made in several ways have been taken from different sources and have been heat-treated to varying hardness by normalizing and by quenching and drawing.   The results, therefore, may be considered to be generally applicable to current engineering steels. A certain limitation with respect to the hardness at which steel should be tested still seems·necessary.   The upper limit of this hardness range has

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been placed at Rockwell B96, as the hardness, tensile-impact, inclusion relation becomes too complex above this hardness to allow its ready use, and extrapolation from the data presented here should not be attempted

MATERIALS, METHODS OF TEST AND EXPERIMENTAL RESULTS

Twenty-nine bars from 19 heats were sampled, inclusions were counted, and midway transverse tensile-impact specimens were tested as normalized and as heat-treated to various hardnesses ranging from 76 to 96 Rockwell B, all the work being carried out in accord with the procedures developed in the preceding study and described in the previous paper   The material was in the form of round and square bars of 2-in to 3-in sections   Transverse tests were used solely rather than in combination with longitudinal tests because the latter vary in the same way but to a smaller degree and are less sensitive.   The amount of testing is thereby cut in half without affecting the nature of the results   It should be emphasized in this connection that tests in the transverse direction represent the worst condition.

Table 1 shows the steels used, the results of the hardness tests, the inclusion count and the tensile-impact values   The heat treatment in each case consisted of oil-quenching ½-in disks, and drawing to suitable temperatures to obtain hardness in the desired range   Normalizing was carried out on full-sized bars   Impact results are the average of two check values, except as noted.   Heats 1 to 8 are the same steels studied previously, and the same nomenclature has been followed

DISCUSSION OF RESULTS

The hardness, tensile-impact values, and inclusion count total length figure of the heats and bars in question as shown in Table 1 are plotted in Fig. 1   In the plotting of this figure, the steels have been divided into three groups with respect to cleanliness   Those containing less than 0.50 mm per sq. mm inclusion length are considered to be cleaner than average, and are shown in Fig 1 as light circles. Those having an inclusion length from 0 50 to 0.70 mm per sq. mm. inclusive, are considered to be of average cleanliness, and are marked by a cross in the graph.   Those containing more than 0 70 mm. per sq mm. total inclusion length are dirtier than average and are indicated in the diagram by dark circles   The dashed line in Fig. 1 is the mean of the steels in question, and shows the tensile-impact strength to be expected from average commercial steel in the hardness range of 76 to 96 Rockwell B.   The full line in Fig. 1 has been arbitrarily selected for purposes of illustration as a division line between steels which would and would not be acceptable for a given application, and, if this line is properly located with

TABLE 1 — *Test Results*

Specimen No [a]	Grade,[b] S A E No	Hardness, Rockwell B	Tensile-impact Strength, Ft-Lb	Total Length of Inclusions, Mm per Sq Mm
11-A	2315	80 0	25 0	0 67
B	2315	76 5	26 0	0 67
C	2315	82 5	26 5	0 67
D	2315	83 0	27 0	0 67
E	2315	84 5	25 0	0 67
12-A	2315	80 0	26 5	0 59
B	2315	83 0	27 0	0 66
C	2315	83 0	25 5	0 66
D	2315	85 5	25 0	0 66
E	2315	88 5	25 0	0 66
13-A	2315	80 0	27 0	0 64
B	2315	79 0	25 5	0 64
C	2315	83 0	25 5	0 64
D	2315	85 5	25 0	0 64
E	2315	88 0	25 0	0 64
21-A	2315	80 0	28 5	0 69
B	2315	80 5	25 5	0 70
C	2315	88 5	25 5	0 70
D	2315	89 0	24 5	0.70
E	2315	95 0	24 5	0 70
22-A	2315	80 0	26 5	0 54
B	2315	86 0	26 5	0 60
C	2315	88 5	25 5	0 60
D	2315	91 0	27 5	0 60
E	2315	94 5	25 5	0 60
31A-A	2315	80 0	27 5	0 45
B	2315	85 5	31 5	0 38
C	2315	88 0	27 5	0 38
D	2315	95 5	24 0	0 38
31B-A	2315	80 0	27 0	0 37
B	2315	85 5	27 0	0 42
C	2315	89 0	27 0	0 42
D	2315	90 5	28 5	0 42
E	2315	93 5	26 0	0 42
41A-A	2315	80 0	23 5	0 64
B	2315	80 5	28 5	0 69
C	2315	83 5	27 0	0 69
D	2315	85 0	20 5	0 69
E	2315	86 5	22 0	0 69
41B-A	2315	80 0	27 0	0 78
B	2315	82 5	28 0	0 70
C	2315	89 0	27 5	0 70
D	2315	91 0	26 5	0 70
E	2315	91 5	24 5	0 70
51A-A	2315	80 0	28 0	0 43
B	2315	82 5	31 5	0 47
C	2315	87 5	28 5	0 47
D	2315	92 0	26 5	0 47
E	2315	92 5	27 5	0 47

TABLE 1 —(Continued)

Specimen No [a]	Grade,[b] S A E No	Hardness, Rockwell B	Tensile-impact Strength, Ft-Lb	Total Length of Inclusions, Mm per Sq Mm
51B-A	2315	80 0	29 0	0 45
B	2315	85 0	27 5	0 41
C	2315	87 5	25 5	0 41
D	2315	88 5	30 0	0 41
E	2315	89 5	26 0	0 41
52A-A	2315	80 0	25 5	0 72
B	2315	77 5	28 5	0 70
C	2315	78 5	25 5	0 70
D	2315	80 5	25 0	0 70
E	2315	87 0	23 5	0 70
52B-A	2315	80 0	24 5	0 79
B	2315	78 0	26 0	0 74
C	2315	84 0	24 0	0 74
D	2315	84 0	26 5	0 74
E	2315	85 0	23 0	0 74
61-A	6130	90 0	20 5	0 71
71-A	6130	90 0	24 0	0 50
72-A	6130	90 0	24 0	0 61
81-A	6130	90 0	18 5	1 02
82-A	6130	90 0	25 0	0 97
91-A	1050	87 0	22 5	0 97
101-A	2340	94 0	23 0	0 64
111-A	2340	94 5	21 0	0 97
121-A	2340	94 0	27 5	0 92
131-A1[c]	3135	93 5	22 0	0 43
A2[c]	3135	92 5	11 0	0 43
141-A	3135	91 5	28 0	0 48
151-A	3135	88 5	24 5	0 88
161-A	4140	93 5	24 5	0 97
171-A	5130	86 0	27 5	0 73
181-A	6120	87 0	23 0	0 80
191-A	6120	92 5	26 0	0 63

[a] Specimens marked A are normalized, all others are quenched and drawn

[b] For convenience the following index to S A E numbers is given The first digit indicates the class of steel, as follows (1) carbon steel, (2) nickel, (3) nickel-chrome, (4) chrome-molybdenum, (5) chrome, and (6) chrome-vanadium The second digit indicates the approximate percentage of the major alloy and the last two digits indicate the carbon content in hundredths of one per cent

[c] Single values

respect to the average line, it would comprise the lower limit for specification purposes.   The dotted line in Fig 1 is included merely for purposes of illustration, indicating an arbitrary division between steels that have exceptionally good tensile-impact values and those that are only average A glance at the diagram will show that in general the extra clean steels

give relatively high values, and the steels that are dirtier than average
give lower than average impact values, although there are many specific
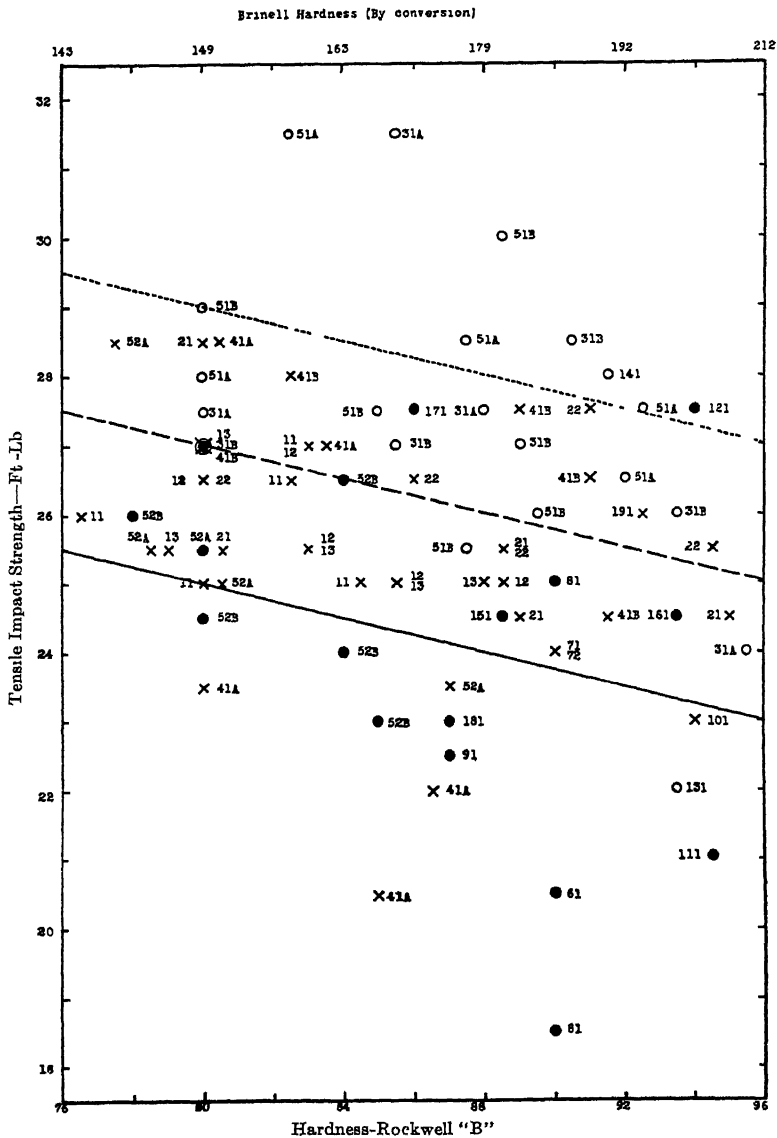
FIG 1 —RELATION OF TENSILE IMPACT STRENGTH TO HARDNESS AND INCLUSION
CONTENT.

○ Low inclusion content   ✕ Average inclusion content   ● High inclusion content.
Numerals next to points are bar numbers

exceptions   The general trend, however, is a satisfactory check of the
work previously carried out and reported in the first paper.

The exceptions to the generalizations above are particularly noteworthy. These exceptions are caused by variation in raw materials, processes of melting and fabricating, microsegregation of inclusions, etc , and it is readily seen that when commercial steels from several sources are considered, the effect of body becomes increasingly important   In Table 2, heats are listed according to cleanliness and body, the latter being determined from the relative location of the points in Fig 1

TABLE 2.—*Summary of Cleanliness and Body*

Heat No	Cleanliness	Body	Heat No	Cleanliness	Body
1	Average	Average	11	Dirty	Average
2	Average	Average	12	Dirty	Good
3	Clean	Average	13	Clean	Poor
4	Average	Variable	14	Clean	Average
5	Clean and dirty	Average	15	Dirty	Good
6	Dirty	Average	16	Dirty	Good
7	Average	Average	17	Dirty	Good
8	Dirty	Variable	18	Dirty	Average
9	Dirty	Average	19	Average	Average
10	Average	Poor			

In this listing of the heats, "average" body is considered as that resulting in average dynamic strength in steel of a given cleanliness   Accordingly, "poor" body is the condition that results in a lower impact strength than would be expected from the cleanliness of the steel   "Good" body is the reverse condition, where the impact strength is higher than indicated by the inclusion content   Although no steels have been listed as dirtier than average with "poor" body, or cleaner than average with "good" body, steels of average cleanliness show variation in body in both directions, and minor variations in both directions are evident in the cleaner and dirtier steels.

This whole matter is illustrated best by specific instances   Of the 19 heats in question, 4 have body better than average, 2 have body less than average, 2 show widely varying body, and 11 heats show average body.   The average inclusion content, average body heats 1, 2, 7 and 19 are seen to lie in the center band of Fig. 1, and the location of a heat outside this band indicates variation in cleanliness or body, or both   Occasionally, cleanliness and body vary inversely, and we have the peculiar condition of a dirty steel with good dynamic strength, or vice versa. Heat 12 is a case in point   This steel, showing the high inclusion count of 0 92 mm , shows an impact strength distinctly better than average The same is true to the same, or slightly lesser, degree in heats 15, 16 and 17.   Again, heat 13 shows better than average cleanliness, but the tensile-impact values are low.   This is the reverse condition, clean steel with poor body.

At this stage of the study, the data show no relation between counted inclusions and body   The only suggestion of any relation between inclusions and body is in the matter of the microsegregation of inclusions Body may well be affected by such microsegregation, and it should cause a marked variation in body in various bars from a heat and even in specimens from the same bar   This condition is typified by heats 4 and 8 Here the specimens show average to poor cleanliness with a wide variation in body, as can be seen from the location of the points in Fig. 1   It is most difficult to separate this factor, microsegregation, from the other factors involved in body   Fortunately, from practical considerations and for specification purposes, this is not necessary   This is particularly true because, from the point of view of service requirements, the heat with widely variable body is just as unsatisfactory as the heat with poor body, and should be treated accordingly   The authors have chosen, therefore, to consider this microsegregation as one of the factors involved in body It should be noted that this microsegregation is of such a nature that sampling error is not involved, and it is not to be confused with macrosegregation, which causes sampling errors   Ingot segregation, as evidenced by the wide variation in heat 5, is of such importance that it should be subjected to a critical study in order to establish a rational system of sampling   Any test, either the inclusion count or the tensile impact, must be based on a standardized, systematic sampling procedure Such a procedure could be worked out by the cooperation of the producer and consumer of the steel

By application of the principles described and the data shown in Fig. 1, it is possible to test any given heat for its relative dynamic strength. To do this, transverse tensile-impact specimens should be prepared as previously described, from material normalized or heat-treated to a hardness of 76 to 96 Rockwell B.   The impact value then obtained may be directly compared to the average as shown in Fig 1.   Moreover, with relatively little more experience, it will be possible to set definite lower limits for specific applications   As both inclusion and body factors are involved, this is a more reliable and satisfactory test of dynamic strength than a count or inspection for inclusions, and should be substituted for the unsatisfactory inclusion rating in specifications intended to establish the dynamic quality of the steel.

CONCLUSIONS

The following conclusions are based on a study of bars 2 to 3 in in diameter, from several heats from different manufacturers, in normalized and heat-treated states, and are believed to apply generally.   The conclusions have been derived from specimens having a hardness range of Rockwell B 76 to 96, and should not be applied beyond this range.

1 The tensile-impact test is a satisfactory test for the determination of the dynamic properties of steel

2. Inclusion content alone is not a satisfactory criterion of the dynamic properties of steel, and may even be misleading

3 The importance of unknown factors comprised in the term "body," as distinct from cleanliness, has been demonstrated

4 A practicable lower limit of transverse tensile-impact strength for specification of the dynamic quality of steel may be selected from the data   Such a definite limit, varying with the hardness, has been selected as an illustration

ACKNOWLEDGMENT

The writers wish to acknowledge the stimulating interest given by Mr J H Critchett, vice president of the Union Carbide and Carbon Research Laboratories, Inc.   They further wish to express their great appreciation of the assistance rendered by their colleagues at these laboratories, and in particular, of the microscopical work by Mr J R Vilella

DISCUSSION

(F N Speller presiding)

J A MATHEWS, New York, N Y (written discussion) —While I am not in complete accord with all of the findings of this paper, it is a paper to stimulate thought and discussion   It is a conscientious effort to add to our knowledge and an attempt to help solve the ever-present question What constitutes the inherent goodness of steel, its individuality and, we might almost say, its personality?

We use many words to express this idea   There is the overworked "quality" and the old Sheffield term "body " There is the new-fangled "timbre," a word borrowed from the French and usually mispronounced so as to suggest the product of the forest industries and perchance to suggest woody structures, and finally, the inelegant but expressive Anglo-Saxon word, "guts "

The authors use the term "body" but arbitrarily eliminate hardness, structure and counted inclusion content from the variables making up "body " It seems to me this is like discussing the human body with spine and legs omitted

The essence of a good definition is that it should mean the same thing to everyone and not be capable of misunderstanding   We have no such definition of "body" as applied to steel   The term, however, is usually considered as applicable to a brand, as such, and certainly to the product of a single heat   As I read this paper, the authors consider it a variable from bar to bar and even from spot to spot in a single bar.   In fact, their conclusions to a considerable extent seem to be predicated upon this concept of "body "

It is hoped that they will supplement their paper with complete analyses of the bars used and state whether electric or open-hearth, basic or acid

We have been told so much about inclusions, of late, that engineers have become inclusion-minded and look upon them as the root of all dynamic evil   They attach photographs to their specifications showing what they want their steel to look like The picture seems to be a photograph of a bathroom tile

It must be remembered that inclusions are normal and most of them are reaction products of the metallic deoxidizers   A piece of runner brick or stopper rod fortuitously included in steel is quite another thing   We can do something about minimizing normal inclusions but we cannot eliminate them so long as metallic deoxidizers are used, or while molten steel erodes spouts and ladles or until the law of mass action is repealed   It is by virtue of this law that the smaller the inclusions the less likely they are to escape in the slag

The difficulty of adopting a transverse tensile-impact test is that it is inapplicable to small sizes, which constitute the bulk of commercial rolled sizes   Moreover, we are only occasionally interested in the transverse qualities of engineering steels, e g , in guns, high-pressure vessels, etc   David Harum said, "When you want to make a house look 'yallar' use 'yallar' paint "   When we are actually interested in transverse qualities there is no doubt that the tensile-impact test, as used by the authors, or the ordinary tangential tensile or impact tests, give us useful information   The question is, does the tensile-impact test give us general information that can be translated into use value of steel for numerous purposes   A careful reading of this and a previous paper by the same authors shows that they are not merely trying to introduce another laboratory test to torment steel makers and consumers, in fact, if their recommended test comes up to their expectations, it is possible that several of the ordinary and older tests might be eliminated with general satisfaction

Having just become inclusion-conscious we note the appearance of many new free machining steels and they are mostly loaded with inclusions   One of the best methods of producing free machining steels was developed by my associate, F F McIntosh   It consists of adding substantial quantities of molybdenum sulfide to the steels   The amount added is usually equivalent to 0 10 to 0 30 per cent sulfur   I am inclined to believe that these steels might not respond favorably to the transverse tension impact test, in fact, when we first made these steels, I was doubtful about their use under conditions involving either fatigue or impact resistance

One of these steels is our Max-el 3½   A straight rotary fatigue test showed a fatigue limit of stress of 76,000 lb for 10,000,000 reversals, and this value is approximately 50 per cent of the ultimate strength of the steel as tested   This is a decidedly good figure   Izod tests show as good or better values for the steel with molybdenum sulfide as compared with the steel free from this addition, over a wide variety of tempering temperatures, when pieces of equal hardness are tested

Our free machining stainless iron No 2 is of the same type   In both wet and dry corrosion-fatigue tests it behaves as well as plain stainless iron of the same carbon and chromium content   In the fully annealed condition the fatigue limit of stress was 58 per cent of the ultimate strength, while plain stainless iron gave a lower ratio   When quenched and tempered at 1200° F , its endurance limit was 57,000 lb , or 54 per cent of the ultimate strength   Plain stainless iron gave 1000 lb higher endurance limit, dry, and equal figures of 41,000 lb were obtained for both grades, wet   Impact tests over the tempering range of 400° to 1400° F show lower but more consistent values over this range but the free machining grade will readily meet the standard requirement of 50 ft-lb Izod for 100,000 lb. ultimate strength   Both of these grades of free machining steel have proved their worth in many applications involving impact and fatigue

Taking these facts into consideration, I feel that we may have to change our thinking about the effect of inclusions on dynamic properties   We may have to distinguish between inclusions of different types or origins   We may have to differentiate between the effects of the different kinds, sizes and numbers—always remembering that most of them are normal constituents

I do not feel that we are warranted in accepting the transverse tensile-impact test as a criterion of quality until further work has been done either by the authors or by a

representative committee to establish the scope or limitations of the test   Probably there are both   As I understand it, the writers feel that the transverse tensile-impact test gives the best cross-section of all properties which are the result of the numerous variables entering into the manufacture and heat treatment of steels   It would be especially interesting to make this test on a chromium-nickel steel subject to temper brittleness, in both the tough and brittle conditions   In that case, the number and size of the inclusions would be the same

F N SPELLER, Pittsburgh, Pa —The effect of inclusions on all physical properties of steel is, of course, the heart of the problem, and investigators are now working on that phase of the subject   It does not follow that the inclusions are always harmful The effect of quantity and size must always be taken into account   We have already found a practical application in controlling the size but not reducing the quantity, and are getting good results in certain operations in the fabrication of steel   So the work will go on and the solution of this particular problem will be watched with a great deal of interest   We may expect some modification of specifications, I suppose, as a result of this work

C H HERTY, JR, Pittsburgh, Pa (written discussion*) —This paper contains some very peculiar conclusions when it is compared with the authors' previous paper (p 143)   In the former paper the conclusion is reached that "the dynamic strength of steels is quantitatively reduced by visible inclusions or factors directly proportional to them "   In the present paper "inclusion content alone is not a satisfactory criterion of the dynamic properties of steel, and may even be misleading "   In spite of these absolutely contradictory conclusions, the first paper concludes that "the tensile-impact test is a satisfactory measure of the dynamic quality of steels," and the second paper concludes that "the tensile-impact test is a satisfactory test for the determination of the dynamic properties of steel "   It is difficult to see how these pairs of conclusions may properly be drawn

With regard to Fig 1   We believe that it is unjustifiable to present eight widely different types of steel on a plot of this kind and attempt to get any consistent relationship   In the first place, most of the points on this plot are the S A E grade 2315   In this the distribution of steels with regard to cleanliness is as follows   Low inclusion content, 19, average inclusion content, 37, high inclusion content, 7   Of the other seven grades, the distribution of cleanliness is   Low nonmetallic content, 3, average nonmetallic content, 4, high nonmetallic content, 9   It would appear to be unnecessary to go further in pointing out the futility of working with the tremendous number of variables which are here present

Finally, although the term "body" may be as apt to solid steel as "catalysis" was to chemistry some 20 years ago, it does seem that we have enough knowledge of ingot structure, macro and micro segregation, solubilities of various materials in steel, factors affecting grain size and carbon precipitation, to talk in more concrete terms than this mysterious "body "

S. L CASE, Pittsburgh, Pa (written discussion).—It is rather difficult to concur with the authors' conclusions on the basis of data submitted by them in this paper On Fig 1 they show tensile-impact strength values plotted against hardness of a wide range of alloy steels, normalized as well as heat treated   The only obvious conclusion which one can draw from these data is that tensile-impact strength generally shows a tendency to slope down with an increase in hardness   The authors' conclusions, however, cover much more territory   These conclusions are based on the assumption

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that tensile-impact strength can be used as a yardstick by which the dynamic properties of steel may be accurately measured   Granting that a tensile-impact test has certain merit as a dynamic test, we have no grounds to assume that the tensile-impact strength reflects the dynamic properties of steel more truly than the elongation and reduction of area, two properties apparently ignored by the authors

The value of any physical test should be measured by the extent to which it can be corroborated by other methods of testing   Before we accept a tensile-impact test as a criterion of dynamic strength, we must assure ourselves that it will answer this requirement   The following may be of interest in reference to this question

During the last few years, the writer has often had occasion to resort to tensile-impact tests in supplementing other methods of testing   Two structural lots of steel on which the actual service performance was known were subjected to a series of static and dynamic tests in the normalized condition   The results are illuminating and are shown in Table 3

TABLE 3 —*Results of Tests on Two Structural Steels*

Steel A	Excellent service record
Steel B	Fabricating trouble and brittleness under shock

CHEMICAL COMPOSITION

Steel	C, Per Cent	Mn, Per Cent	P, Per Cent	S, Per Cent	Si, Per Cent
A	0 21	0 41	0 018	0 030	0 02
B	0 20	0 37	0 018	0 033	0 02

STATIC TENSILE TESTS

Steel	Yield Point, Lb per Sq In	Tensile Strength, Lb per Sq In	Elongation in 2 In , Per Cent	Reduction of Area, Per Cent
A	35,140	62,150	25 7	57 1
B	34,790	61,840	26 5	57 7

IMPACT TESTS

Steel	Tensile-impact Tests			Izod Impact Bend Tests, Ft-lb	Repeated Impact Tests, Height of Drop 2 In
	Impact Strength, Ft-lb	Elongation in 2 In , Per Cent	Reduction of Area, Per Cent		
A	26	33 3	61 3	78–77–73	1648 blows
B	27	37 4	66 2	42–46–32	1102 blows

It is obvious that in this case the tensile-impact strength did not give any indication of the true dynamic properties of the steel   In numerous other instances bessemer steel displayed considerably higher tensile-impact strength than corresponding open-hearth grades   Should we assume, then, that bessemer steel has better dynamic properties than open-hearth steel?   Are we justified in assuming, for instance, that steel 51B-A, shown on Table 1, is greatly superior to 22-A simply because it has a tensile-impact strength of 29 ft-lb as against 26 5 ft-lb for 22-A?   Incidentally, on

most of the tests tabulated on Table 1 the normalized specimens show a higher tensile-impact strength than the quenched and drawn specimens   Does this imply that in the normalized condition steel has dynamic properties superior to the quenched and drawn state?

In their conclusion 1 the authors state that ' the tensile-impact test is a satisfactory test for the determination of the dynamic properties of steel "   This conclusion is not supported by any evidence in the text   Failure to prove it leaves conclusions 2, 3 and 4 without tangible support

A B KINZEL AND W CRAFTS (written discussion) —It is always a privilege to receive a discussion from Dr Mathews, and in this case it is a particular pleasure in that we agree with practically all of the points which he has stressed, and are very glad to have him emphasize some of the things which we brought out less forcibly in the paper

The use of the term "body" is not new in steel metallurgy but despite its long common usage no adequate definition has been forthcoming   It has seemed to us that in using the term the steelmaker implies that it is a sum total of those things about which he knows little or nothing   Thus in our former paper of the same title we defined the term as that characteristic of a steel which enables it to have more resistance to dynamic stresses than would be expected from the physical properties on static test or from the apparent cleanliness or lack of cleanliness of the steel   This of course is a matter of terminology and, while the term "body" is not as elegant as we might wish, we know of no other method of expressing the characteristics involved   This use of the term "body" might well be applied as a brand, because steel of the same brand in different states of heat treatment would have different physical properties and still show the extra characteristics implied   This would be evidenced in general on the whole heat but there might well be minor variations in different ingots of the heat, different parts of the ingot and even in different places in a single bar   This is due to the very nature of the factors involved in the term "body," such as microsegregation and other little known factors   The complete analysis of the bars used and their mode of manufacture have been purposely omitted because the steels were given to us in confidence, and if these data were given they might easily be used for purposes for which they were never intended   It is of interest, however, that we could find no difference in the body of the basic and open-hearth steels involved   The overemphasis of inclusions in steel by many engineers and the failure to appreciate that inclusions are a normal, integral and inherent part of steel is well brought out in Dr Mathews' discussion, and we concur with him heartily in these opinions   The limitations of the transverse tensile-impact tests with respect to commercially rolled bars, many of which are less than $1\frac{3}{4}$ in in transverse dimension, have been recognized, and we are even now working on the use of a specimen which can be taken transversely from a 1-in bar and which should give results identical with those obtained on the longer specimen   We cannot agree with Dr Mathews that we are only occasionally interested in the transverse qualities of engineering steels   It is true that the outstanding examples of structures in which this property is of prime importance are guns and pressure vessels   However, gears, axles working in torsion and rolled steels used where shock is involved are unquestionably subjected to high transverse stress, and the resistance to this transverse stress must play a considerable role in the performance of such pieces, particularly if this resistance is such as to come under the category of the weakest link in the chain of properties   Moreover, practically every structure in which bending moments are involved is subject to high transverse stress due to the normal tangential component of the longitudinal stress   Thus it seems to us that this property is brought into play in many more applications than would at first be anticipated   Dr Mathews very rightly points out that we believe that the transverse impact test is more logical than many of the tests now applied and

that it is our purpose not to torment steel makers and consumers with another test but rather relieve them of some of the less logical and burdensome tests under which they are now laboring   The argument with respect to "yellow paint" is unquestionably sound, and we believe that the test herein proposed is not at variance with this doctrine   It should, of course, be intelligently applied and Dr Mathews' illustration of free machining steels loaded with inclusions is a good illustration of how it could be misapplied   There is little doubt that these steels would show low transverse impact test results, and it would be folly to condemn them on this ground for use in applications where this property is unimportant   If the steel were used in an application where the property was important, we feel sure that the verdict given by the transverse tensile-impact test would be substantiated by service   As yet we have not had the opportunity to test the chrome-nickel steel subject to temper brittleness, but believe that this would be an interesting case and hope to perform this test in the near future   We agree with Dr Mathews that before we have a reasonably complete understanding of the various phenomena involved we must be able to distinguish between the effects of different types of inclusions, or inclusions of different origins, as well as the effect of the sizes and distribution   Such knowledge would unquestionably go a long way towards clearing up the various unknown factors involved in the term "body, ' and as the science progresses such information will no doubt be forthcoming, in fact, our present work is an effort in this general direction, but the whole problem is so complex that the best we can do at the present time is to use some indicator which will give us the integrated effect of all of the facts involved   We propose the transverse tensile-impact test as such an indicator   The work herein described shows that it is worthy of further consideration   We agree with Dr Mathews that there is still much work to be done, but believe that the test has now reached the stage where a direct application and correlation of service data is in order

We cannot agree with Dr Herty as to the conclusions in this paper being contradictory to anything which we have as yet published on the subject   It is consistent and logical to make simultaneously the statements that inclusions quantitatively affect the dynamic strength and that other factors in the steel may have still greater effect on the dynamic strength   The first statement makes no reference whatever to the absolute effect of the inclusions, and holds, regardless of whether this effect is relatively large or small   It is also logical and consistent to state that regardless of whether or not the inclusion effect is large or small compared to other factors, the transverse impact test gives the integrated effect of all the factors involved   In Fig 1, as Dr Herty points out, many of the steels were grade 2315, and the remainder were of grades chosen at random   It is legitimate to place these on the same plot because not only do the two groups check each other with respect to the inclusions and body effects but it was our immediate purpose to show that the relationships are general in character   The only way to handle the immense number of variables present is to group them in terms of unknown and known, and it is precisely the effect of the unknown variable which we have studied here   Dr Herty's statement that it is futile to work with such a great number of variables is directly in contradiction to his next statement to the effect that we seem to have enough knowledge of ingot structure, segregation, etc , etc , to handle it quantitatively   If such knowledge were available, it would certainly not be futile to work with this number of variables   We regret even more than Dr Herty that the state of knowledge at the present time absolutely precludes quantitative consideration of the various factors involved in the term "body "   The fact that this task has never even been started is sufficient proof of our general lack of knowledge, and shows the necessity for an empirical test for the dynamic properties of steel   Even now specifications involving "body" are being written, and it is not infrequent for an engineer to specify analysis, brand or

performance   In effect, when specifying brand, he is specifying body by V, and when specifying performance, he is requiring high body characteristics

The discussion by Mr Case is fundamental in character and presents in a succinct form the possible objections to the tensile-impact test   We believe, however, that these objections have been and can be satisfactorily answered   The relation between tensile-impact strength and hardness is allowed by Mr Case   He then compares tensile-impact value with the elongation and reduction of area as a measure of dynamic strength   So much regarding the elongation and reduction of area in static tests has been written that we take it that Mr Case means elongation and reduction of area in the impact test   In this connection we might point out that both of these properties were carefully studied and reported in the original study of this subject (p 143), referred to in this, the second paper   We have found them to be quite satisfactory as a measure of dynamic performance but no more so than the tensile-impact strength itself and, as the latter is more readily obtained and is more accurate, we have chosen this for our further studies as reported in this paper   Mr Case states, as a premise, the thought that the value of any physical test should be measured by the extent to which it can be corroborated by other methods of testing   We disagree with this principle and believe rather that the value of any physical test should be measured by the extent to which it can be correlated with service data   If dynamic tests could be correlated with static tests, there would be no point in carrying out dynamic tests   The illustration given by Mr Case is very interesting   However, no mention is made of the fact that this test was performed on transverse specimens and, from the appearance of the data, it seems highly probable to us that this tensile-impact test was performed on longitudinal specimens   There is a marked difference in behavior of the tensile-impact tests taken longitudinally and transversely, as discussed in the previous paper already mentioned   The Izod and repeated impact tests quoted by Mr Case are interesting, but it should be remembered that in each of these tests a notch or its equivalent is used   Steel used in service either does not or should not contain notches   Fillets are usual and, where fillets are not in use, difficulty is generally experienced even though steel with the best dynamic qualities is employed   Thus, what we are interested in from the service standpoint is not only the rate of propagation of a notch, as measured by the tests quoted by Mr Case, but rather the probabilities of formation of a notch as well as its rate of propagation   Experimentation indicates that this combination of properties is satisfactorily measured by the transverse tensile-impact test   Thus, Mr Case's argument that his longitudinal impact test did not give any indication of the dynamic properties of the steel is correct but not pertinent, as the transverse impact test is recommended, and not the longitudinal impact test.   Wrought iron gives excellent longitudinal impact tests, and we are not surprised that bessemer steel has been found to behave in the same way   Regarding the steels 51B-A and 22A in the table, the position of 22 shows definitely that we would consider it an entirely satisfactory steel for service, although 51 is somewhat better   No mention is made of the fact that 51 is greatly superior to 22   Mr Case believes that Table 1 shows normalized specimens to have higher tensile-impact strength than quenched and drawn specimens.   A careful perusal of this table, with proper correctons for differences in hardness according to the hardness-tensile impact relation, fails to show any such trend   It should be remembered that the experimental error is approximately 5 per cent of the final value and that a difference of 80 to 90 Rockwell hardness corresponds to a difference of 2 ft-lb   The work done and reported in the first paper (p 143), together with that in the present paper, shows definitely that the transverse tensile-impact test measures the combination of properties of the material, which enables it to resist notch formation as well as notch propagation, and this seems to be the most logical combination of properties to test from the service standpoint   We thus believe that contrary to Mr Case's

opinion, conclusion 1—that the dynamic strength is indicated by the tensile-impact test—is well founded both on logical and experimental evidence   Conclusions 2 and 3 are quite independent of conclusion 1, so that any criticism of conclusion 1 does not involve conclusions 2 and 3, as Mr Case would have it   The specification of dynamic strength in conclusion 4 is directly related to conclusion 1, and the plot in Fig 1 shows that this last conclusion is in line with experimental data

We particularly wish to thank Mr Case for presenting in such a striking and pertinent fashion the arguments against the tensile-impact test

Method for Electrolytic Extraction of MnO, MnS, FeS and SiO₂ Inclusions from Plain Carbon Steels*

method or some entirely new procedure will be developed for alloy steels Some work is being done in this direction at the present time

Ferrous and ferric hydroxides and basic ferric sulfate contaminate the inclusion residue   If it were not for this fact, a determination of FeO could be made by this method, because FeO is absolutely insoluble in the electrolyte   An entirely different method is being developed at present, which will probably determine the quantity of this oxide that is present in plain carbon steels

The method about to be described will determine satisfactorily the percentage of manganese-containing inclusions (MnO + MnS), FeS, silica (SiO_2) and alumina (Al_2O_3).   A tentative procedure is outlined for the separation of MnO from MnS, which is being critically surveyed and which appears to be satisfactory.

Neither time nor space can be devoted to all the data on hand which substantiate the use of this method   The complete information is being prepared for publication[1] and will appear in the near future   The description which follows should be sufficient to enable one to install and operate the method

BRIEF OUTLINE OF ELECTROLYTIC PROCEDURE

The mechanism of this procedure specifies that the steel sample be electrolytically dissolved in a ferrous sulfate solution.   The specimen is separated from the main body of electrolyte by means of a dializing medium (collodion bag).   The pores of this membrane are large enough to allow the passage of the iron ions through its walls and yet are extremely small in comparison with the inclusions, even those of submicroscopic size. Therefore, as these particles fall from the electrolyzing sample they are retained by the bag and subsequently may be analyzed   Hence it may be seen that the purpose of this method is not to plate iron on the cathode, but to ionize the iron and pass it through the collodion membrane, while the inclusions are retained inside the bag   Some of the mistakes made in applying this procedure have occurred through the desire to obtain a deposit of good appearance on the cathode   One should not care whether the iron plates well or gives all hydroxides, as long as the inclusions inside of the bag are not dissolved or contaminated with materials that will hinder their correct analysis.

The important factors upon which the success of this method depends are described in detail in the following pages

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[1] G R. Fitterer, B E Sockman, W E. Marshall, R B Meneilly and E. A. Krockenberger Development of a Method for Electrolytic Extraction of Oxides and Sulphides from Plain Carbon Steels   U S Bur Mines *Rept of Investigations* (in preparation).

The Electrolytic Cell

The type of apparatus now in use at the Pittsburgh Experiment Station of the U. S. Bureau of Mines is illustrated in Fig. 1. Three of these cells are in operation; each consists of a copper tank (A, Fig. 1) which is 20 in. long and 7 in. square and has a capacity of approximately 14 liters. This copper box serves as the cathode during electrolysis and the electrolyzed iron is plated on its inside walls. A copper bus bar D, 1 in. wide and $\frac{1}{8}$ in. thick, is suspended lengthwise above the center of the tank, from which it is insulated, since it serves as the anode upon
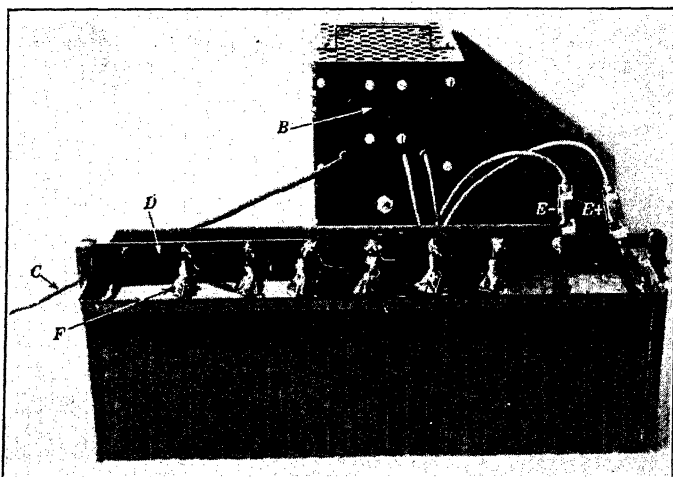
FIG. 1—MULTIPLE ELECTROLYTIC CELL WITH SIX SAMPLES IN POSITION.

A. Copper tank.	$E-$. Negative terminal.
B. Battery charger.	$E+$. Positive terminal.
C. Supply line.	F. Samples.
D. Bus bar	

which the steel samples are suspended during electrolysis. Seven wing nuts are evenly spaced $2\frac{1}{2}$ in. apart along this bar. It is important also that the end nuts shall be about 3 in. from either end wall of the tank. One sample (F, Fig. 1) is suspended from each of these nuts. The present equipment at the Bureau has connections for about 21 samples.

The Electrolyte

A solution of 3 per cent of $FeSO_4.7H_2O$ and 1 per cent of $NaCl$ in water serves as the electrolyte. It is important that the volume of electrolyte be kept so that there are approximately 2 liters per sample. In no case should the volume be less than 1 liter per sample.

Another important factor which should be observed is that the steel sample should never be so large in proportion to the volume of the collodion bag that little room is left for the filtered electrolyte. Approxi-

mately 50 to 100 c c. of electrolyte should be present with each sample in every collodion bag.

As will be shown in the more detailed report, this solution has several advantages as well as some disadvantages, and it is pertinent that the advantages are quite sufficient for its use   The chief advantage lies in the fact that the hydrogen-ion concentration of the solution as prepared is 10^{-3} but after 3 hr of electrolysis it decreases to 10^{-7}, at which value it remains throughout the electrolysis   Hence the solution is chemically neutral during the major portion of the electrolytic run (24 hr).

The chemical neutrality of the solution constitutes the chief advantage of this method over any other yet proposed, because no dissolving effect on the inclusions is exhibited   In spite of this neutrality, the steel sample is rapidly dissolved by electrolysis   The freshly prepared solution may be neutralized before the regular samples are dissolved, by electrolyzing several bars of steel for 2 to 3 hr without collodion bags

Voltage and Amperage

The potential across the electrodes should be maintained between 3 and 5 volts   The current is usually 1 amp. per sample and in each of the three 7-sample tanks described above, 7 amp are used.   One ampere per sample will electrolyze very nearly one gram of steel per hour—the theoretical amount   At least 20 g of steel should be electrolyzed, and 24-hr runs are quite convenient after the procedure has become routine. The present output of this method at the Bureau is from 16 to 20 samples every 24 hr (a total of approximately 500 g. of steel dissolved), with two analysts working on the samples   This routine may be continued indefinitely   Some 2000 samples have already been electrolyzed and analyzed in these laboratories

The source of current for each tank is one 110-volt a c. (supply line C, Fig. 1) Westinghouse Rectox battery charger (B, Fig 1).   These deliver from 5 to 7 amp direct current at about three volts   The negative terminal of the charger $E-$ is connected to the copper tank and the positive terminal $E+$ is attached to the bus bar D upon which the samples are suspended   Any other source of supply will suffice as long as it consistently delivers 1 amp per sample at this or a little higher voltage Some laboratories that are using this method have a supply of 110 volts d c , which is changed to the desired voltage and amperage by a lamp bank series of resistances

Preparation of Sample

The steel specimen should weigh at least 50 g , because it is never electrolyzed to completion.   Also, it has been found that at least 20 g should be electrolyzed in order to minimize the analytical error.   The sample may be as large as desired, provided, of course, that the cell and

collodion bags are made in proportion. It is preferable that the sample weigh from 100 to 200 g. and that it be cut long and narrow. The usual sample at the Bureau is ¾ by ¾ by 3 in. All of the oxide scale should be ground or machined from the surface of the specimen, and the corners and edges should be beveled as shown in Fig. 2, so as to not cut the collodion bag. The specimen E (Fig. 2) is suspended from the bus bar D (Fig. 1) by means of a 22-gage platinum wire A (Fig. 2), which is soldered with the usual lead-tin solder D on to one end of the sample. A loop or kink C is made about halfway up the wire and supports a small
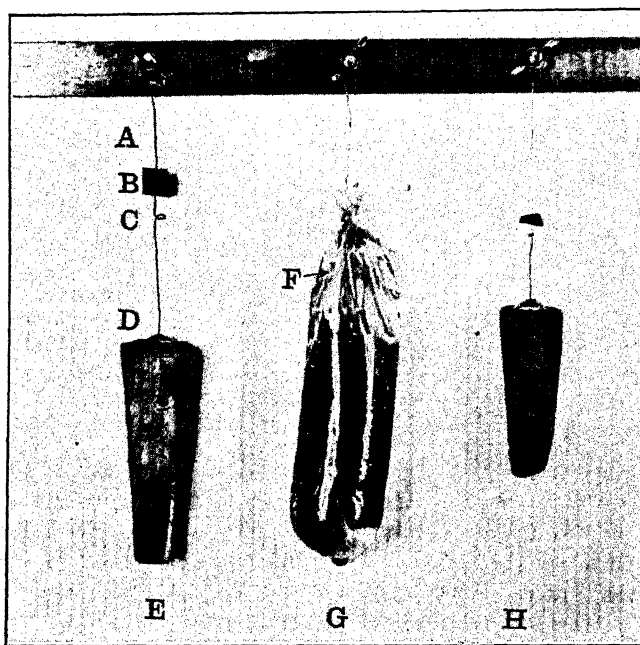
FIG. 2.—PREPARATION OF SAMPLE FOR ELECTROLYSIS.

A. Platinum wire.	E. Sample.
B. Rubber stopper.	F. Collodion bag.
C. Loop of wire.	G. Sample completely prepared.
D. Lead-tin solder.	H. Dry electrolyzed sample.

piece of rubber stopper B. This serves as a support for the collodion dializing bag F, the open end of which is gathered together and tied above the rubber block.

THE COLLODION BAG

A thin collodion bag F is the membrane through which the iron ions pass in traveling to the cathodic walls of the tank, and in which the sulfides and oxides are retained as they fall from the electrolyzing sample. This bag is prepared by pouring a collodion solution into a large test

tube (1½ in inside diameter and 7 in long)   The tube is rotated so that the collodion wets the entire inside wall   The excess is then drained off thoroughly   If an air blast is available, air is blown into the tube, at a low pressure at first then with gradually increasing pressure, up to 3 to 4 lb per sq in , as the collodion dries   As soon as possible the film is loosened around the edges of the tube with the finger nail and if the air is blown down between the tube and the film, the bag may be instantly loosened and pulled out of the test tube   If no air blast is available, the tube is rotated and dried by natural evaporation and after the edges of the bag have been loosened a stream of water directed between the tube and the film will facilitate the immediate removal of the bag   An air blast is preferable to the second method, because it is much faster and the tube does not have to be dried before another bag can be made.   One precaution which cannot be overemphasized is that the bags should not be too thoroughly dried out by the air blast   The bag should be removed from the tube just as soon as the underneath portion has ceased to be liquid enough to make a weak spot in the film

As soon as a bag is prepared, it is submerged in water until used, and it is preferable to use the bags within a few hours after they have been prepared   Observation of these factors will result in a pliable film and a permeable membrane for the electrolysis, whereas a dried-out bag will cause trouble

The collodion solution in use at the Bureau is Mallinckrodt U S P — 4 per cent collodion, 24 per cent alcohol, and 72 per cent ether.   In buying this material, it is specified that no plasticizer such as camphor oil shall be present, as such materials are highly detrimental

THE ELECTROLYSIS

The clean dry sample, including the solder, the platinum wire, and the rubber block E, is first weighed and then suspended on a ring stand and clamp about 10 in above the top of the laboratory table.   A freshly prepared collodion bag is then partly filled with 50 to 100 c.c of filtered electrolyte.   If desired, the solution may be obtained from the tank and filtered.   The bag is then brought up and around the suspended sample   The open end of the bag is gathered together and tied with a strong thread just above the little rubber block B

The bag, with its enclosed electrolyte and sample, is immersed in the tank solution until only ½ in. of the bag shows above the surface.   The platinum wire is then fastened to one of the wing nuts on the bus bar.   A sample which has been completely prepared for electrolysis is shown at G, Fig 2   One should be certain that in letting the bag down into the tank there is from 1½ to 2 in between the bottom of the tank and the bag.   If this space is too small, bridging across the electrodes may result, which causes a surge of current through the sample, exceeding its limiting

current density and causing it to become passive   The conduction of current through this sample will then be inhibited and no more of the sample will be dissolved   Usually a sample of this type will electrolyze about 4 g in 24 hr at 1 amp , showing that probably it electrolyzed for 3 to 4 hr., then became passive and stopped electrolyzing

After the seven samples are placed in bags and set in position in the cell, the current is turned on and the cell requires no more attention for the next 24 hr   During the electrolyzing period, the chemists have time to analyze previously electrolyzed samples, prepare collodion bags and solder the platinum wire to the next samples to be studied

At the end of the 24-hr period, the current is shut off and the samples are lifted from the electrolyte   The outsides of the bags are rinsed off with distilled water and each sample is placed in a separate beaker[2] of 400 to 600 c c capacity   The collodion bags are now untied and split lengthwise from top to bottom   All of the residue is washed from the inside of the bag with a stream of water from a wash bottle, and the pieces of the bag are then thrown away

The sides and ends of the remaining sample are scraped with a rubber "policeman," and the residue is washed off with distilled water   After the samples have been thoroughly cleaned, they are set to dry in the air blast, while the inclusions are separated from the electrolyte by filtering on a No 42 9-cm paper through a Buchner funnel (3 in inside diameter) A suction pump is used and the residue is washed six times with warm distilled water.   The inclusion residues are now ready for analysis

The dry electrolyzed samples with their wires, etc (similar to the one shown at H, Fig 2) are now reweighed so as to determine the amounts electrolyzed by comparison with their previous weights

ANALYTICAL PROCEDURE FOR DETERMINATION OF MnO AND SiO$_2$ IN EXTRACTED INCLUSIONS

The residue on the filter paper contains Fe(OH)$_2$, Fe(OH)$_3$, FeO (not determined by this procedure), graphite, FeS, MnO, MnS, SiO$_2$ and Al$_2$O$_3$ The paper is dried, folded, placed in a clean platinum crucible and ignited for one hour at a low temperature (just sufficient to ignite the paper).

Determination of SiO$_2$

The residue is fused with 5 to 10 g of Na$_2$CO$_3$ (anhydrous).   Blank determinations should be run on this material so as to insure that it is not contaminated with any of the oxides which constitute the inclusion material.

After the fusion has been kept molten for about 10 min , it is run up on the sides of the crucible or poured on to the crucible lid and allowed to

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[2] At this time the other samples which have been prepared are set in place in the cell and electrolysis is started.

cool   It is then leached with 1·1 HCl in a casserole and dehydrated with
5 c c of H_2SO_4.   After baking for some time, the dish is allowed to cool,
HCl (1 1) is added, and the mixture is heated slowly until all of the salts
are in solution   After it has been brought to a boil, the solution is filtered
(filtrate A) through a No. 40 9-cm paper, washed thoroughly, placed in a
platinum crucible, ignited and weighed.   The residue in the crucible is
then treated with 3 to 4 drops of concentrated H_2SO_4 and 2 to 5 c c. HF
After fuming on a·hot plate, the sample is ignited in the muffle for a few
minutes and reweighed   The loss in weight represents the amount of
silica present in the extraction, and the percentage of SiO_2 in the steel may
be determined directly according to the following simple relation·

$$\frac{\text{Grams } SiO_2 \text{ (as determined above) } \times 100}{\text{Grams steel electrolyzed}} = \text{per cent } SiO_2 \text{ in steel}$$

Determination of Al_2O_3

In many steels it is unnecessary to determine the Al_2O_3 content, when
little or no aluminum was used for deoxidation   Also, it is probably
more desirable to determine this oxide quantitatively by the direct HCl
method [3]   When aluminum is the predominant deoxidizer, the direct
method is satisfactory, but when aluminum is used in conjunction with
manganese and silicon in amounts above 0 50 and 0 10 per cent, respec-
tively, Al_2O_3 should be determined on the electrolytic residue.   When it
is necessary to determine Al_2O_3 in this residue, it is convenient to use
one of the following methods, depending upon the conditions encountered:

1. The separation of the iron from the aluminum hydroxide with an
excess of NaOH (described below)

2 The phosphate method [4]

3. The ignition of iron and aluminum hydroxides and the separation
of iron by titration [5]

The method that is generally used at the Bureau is the NaOH sepa-
ration.   The filtrate A from the silica analysis is acidified with 5 to 10
c c. of HNO_3 and boiled.   Cool and precipitate the iron and aluminum
with a very slight excess of NH_4OH.   Settle, filter (filtrate B), wash
well with warm water   Dissolve the precipitate with slight excess of
HCl and dilute to 300 c c   Add 20 per cent solution of NaOH until the
iron hydroxide is precipitated, then add 10 c c. of NaOH solution in

[3] C H Herty, Jr , J M Gaines, Jr., H Freeman and M. W Lightner A New
Method for Determining Iron Oxide in Liquid Steel   *Trans* A I. M E , Iron and
Steel Div (1930) 28–38.

[4] C H Herty, Jr , C F. Christopher and R W Stewart The Physical Chemistry
of Steel-making· Deoxidation with Silicon in the Basic Open Hearth Process   *Bull.*
38, U S Bur. Mines, Carnegie Inst of Tech and Mining and Metallurgical Advisory
Boards (1930) 99

[5] *Ibid* , 102

excess   Heat, so as to coagulate the iron hydroxide and insure the solution of the aluminum hydroxide   Settle, filter while hot (filtrate C), and wash well with warm water   Filtrate C contains the aluminum Make slightly acid (to litmus) with HCl and then make very slightly alkaline (to litmus) with $NH_4(OH)$ Boil to coagulate the aluminum hydroxide, filter, wash well with warm water   Burn off the residue in a weighed platinum crucible.   Add from 2 to 5 c c HF and 2 to 3 drops of concentrated H_2SO_4 Heat on hot plate until fumes of SO_3 are given off, then ignite at high temperature in a muffle furnace until a constant weight is obtained   Reweigh the crucible so as to determine the weight of Al_2O_3 present   Hence

$$\frac{\text{Grams } Al_2O_3 \times 100}{\text{Grams steel electrolyzed}} = \text{per cent } Al_2O_3 \text{ in steel}$$

Determination of $(MnO + MnS)$

When an Al_2O_3 analysis is not required, the analysis for the manganese-containing inclusions $(MnO + MnS)$ is made on filtrate A from the silica determination [6]   Add to filtrate A (or B[6]) 15 c c. of concentrated HNO_3 and 10 c c of concentrated H_2SO_4.   Place this solution on the hot plate until the chlorides are removed and fumes of SO_3 are given off.   Then add about 100 c c. of HNO_3 (25 per cent by volume) and heat the solution until all of the residue has dissolved.   Cool and add 0 5 g of sodium bismuthate   Rotate the contents of the beaker and heat until the pink color has disappeared.   Cool, and if precipitated MnO_2 is present add crystals of $FeSO_4$ until the solution becomes clear.

Boil for 2 min to remove the oxides of nitrogen, and cool in ice water Now add 2 to 3 g of sodium bismuthate and stir the contents of the beaker for 5 min   Dilute with 50 c c of 3 per cent HNO_3 and filter through asbestos.   Wash the residue with 50 c c of 3 per cent HNO_3.   The filtrate should be clear although colored, and absolutely free from undecomposed bismuthate

The pink color of the solution is reduced to a pale yellow by the addition of an excess of standard ferrous sulfate solution (approximately 0.05 N).   The pink end point is then titrated back with the standard permanganate solution (approximately 0.05 N)

The gram equivalent of manganese in the filtrate may then be calculated to grams of MnO.   Hence

$$\frac{\text{Grams MnO} \times 100}{\text{Grams steel electrolyzed}} = \text{per cent MnO in steel}$$

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[6] When an Al_2O_3 analysis is required on the electrolytic residue, the manganese-containing inclusions are determined by analysis of filtrate B as given in the Al_2O_3 procedure.

It must be recalled here that this value contains both the oxide and sulfide of manganese and probably should be spoken of as "manganese-containing inclusions calculated to MnO "

Separation of MnO and MnS (Tentative)

A tentative procedure for the separation of MnO from MnS has been devised   It has been found that MnO is soluble in a 50 50 mixture of electrolyte and sodium citrate (250 g citrate per liter). If a separation is desired, the electrolyte which remains in the collodion bag with the electrolyzed sample is diluted with an equal portion of citrate solution and held at 80° C for 1 hr   This dissolves any MnO that may be present, while the MnS remains insoluble   This solution may then be filtered, the residue ignited, fused with sodium carbonate and carried through the procedure for manganese described above   The manganese obtained in this case is MnS and should be calculated to percentage in the steel

Hence, if a previous determination of the "total manganese-containing inclusions calculated to MnO" has been made, this separated MnS may be calculated to MnO and the difference

$$\left(\begin{array}{c}\text{Total per cent Mn inclusions}\\ \text{in steel calculated to MnO}\end{array}\right) - \left(\begin{array}{c}\text{Per cent MnS in steel}\\ \text{calculated to MnO}\end{array}\right) =$$
$$\text{Per cent MnO present}$$

Also, knowing the amount of MnS present, the amount of FeS may be calculated:

$$\left(\begin{array}{c}\text{Total S (according to regular}\\ \text{steel analysis)}\end{array}\right) - \left(\begin{array}{c}\text{S as MnS as determined}\\ \text{above}\end{array}\right) =$$

Per cent S in steel as FeS, and per cent FeS = per cent $S_{(FeS)} \times \dfrac{87\ 84}{32}$

Incidentally, the electrolytic method recovers all of the sulfur in the steel and a sulfur determination on the electrolytic residue calculated in terms of the grams of steel electrolyzed will check the ordinary sulfur determination on the steel drillings. In other words, both MnS and FeS are in the electrolytic residue. The MnO-MnS separation is questionable in steels containing manganese silicates, since it is difficult to break down the silicate by leaching. However, this separation may be used in a great number of steels which do not contain manganese silicates

PRECAUTIONS

The procedure described above is extremely simple when properly installed, but the experiences of various plant laboratories have shown that many minor mistakes may be made in its application   These failures have been reviewed, their causes determined, and the following

list of precautions prepared so as to emphasize these factors for the future operator.

1   The tank should contain 2 liters of electrolyte per sample

2   The collodion bag should contain 50 to 100 c c of electrolyte

3   The collodion bag should be freshly prepared on the day of its use and should be kept under water until used

4   The collodion bag should be so placed in the copper tank that it is at least 2 in from the side or end walls and the bottom of the tank

5   The top of the bag should not extend more than $\frac{1}{2}$ in. above the top of the electrolyte

6   The electrolyte should not be used more than three times

7   The electrolyte should be neutralized by electrolyzing 3 to 4 samples of steel simultaneously (without bags), before the regular samples are connected

8.   The testing should be organized in such a manner that when the bags from a previous run are removed from the cell, new samples in bags may be fastened in place without the loss of more than an hour   Otherwise, the hydrogen-ion concentration of the electrolyte will increase and basic ferric sulfate will precipitate.

9   The voltage across the electrodes should be approximately 3 to 5, and the current should be approximately 1 amp per sample (not more than 1 5 amp per sample).   This should dissolve about one gram of steel per hour

10.   The sample should not be electrolyzed until very little other than the solder remains on the wire, because lead sulfate and tin chloride will form   Also, chlorine gas will be given off inside the bag, the solution will heat up, and general contamination of the inclusions will result.   However, if samples of the size specified above are used (100 to 200 g), absolutely no trouble results from the solder and it appears exactly the same after the electrolysis as it did before.

TYPES OF RESULTS OBTAINED

Table 1 gives some results obtained by the electrolytic method on various grades of steel   In testing high-manganese, high-silicon steels (1.50 per cent Mn and 0 20 per cent Si), difficulty due to contamination of the residue with metallic particles has been met.   Further research on this grade of steel is necessary before the method can be applied to it

CONCLUSION

It is hoped that the idea has not been conveyed to the reader that this analytical method has many difficultly controllable variables.   On the contrary, after the process is properly installed the procedure is surprisingly simple and the results obtained more than warrant its use   Some

TABLE 1.—*Types of Results Obtained by the Electrolytic Method*

Type of Steel	Sample No.	Deoxidation	Analysis of Steel, Per Cent					Laboratory	Electrolytic Extraction, Per Cent			
			C	Mn	P	S	Si		SiO₂	MnO (MnO+MnS)	Al₂O₃[a]	.Al₂O₃[b]
Basic open-hearth..........	1	Mn only (rimmed steel)	0.07	0.33	0.025	0.03		Bur. Mines	0.004	0.025		0.004
Basic open-hearth..........	2	Mn only (rimmed steel)	0.07	0.33	0.025	0.03		Bur. Mines	0.004	0.030		0.005
Basic open-hearth..........	3	Mn only (rimmed steel)	0.07	0.33	0.025	0.03		Bur. Mines	0.004	0.031		0.006
Basic open-hearth..........	4	FeSi and FeMn	0.23	0.65	0.033	0.028	0.28	Bur. Mines	0.060	0.064	0.004	
Basic open-hearth..........	5	FeSi, FeMn, Al	0.23	0.65	0.033	0.028	0.28	Bur. Mines	0.030	0.057	0.039	
Basic open-hearth..........	6	Spiegel and Mn in furnace; FeSi in ladle	0.40	0.60	0.02	0.03	0 15	Bur. Mines	0.020	0.062		
Basic open-hearth (center of ingot).........	7	FeMn, FeSi and Alsifer in ladle	0.40	0.60	0.02	0.03	0.15	Bur. Mines	0.045	0.045		0.032
Basic open-hearth (center of ingot).........	8	Recarburized; FeMn and FeSi in ladle	0.40	0.60	0.02	0.03	0.15	Bur. Mines	0.031	0.108		
Basic electric plain carbon low-manganese tool	9	Ferrosilicon	1.04	0.16	0.015	0.011	0.21	Bur. Mines	0.019	0.007		
	9	Ferrosilicon	1.04	0.16	0.015	0.011	0.21	Plant	0.022		0.013	0.007
Basic electric plain carbon low-manganese tool	10	Ferrosilicon	1.10	0.23	0.008	0.012	0.36	Bur. Mines	0.022	0.008		
Basic electric plain carbon low-manganese tool	10	Ferrosilicon	1.10	0.23	0.008	0.012	0.36	Plant	0.020		0.005	0.005
Basic electric plain carbon low-manganese tool	11	Ferrosilicon	1.09	0.23	0.007	0.011	0.27	Bur. Mines	0.040	0.007		
Basic electric plain carbon low-manganese tool	11	Ferrosilicion	1.09	0.23	0.007	0.011	0.27	Plant	0.040		0.009	
Krupp..........	12	Carbon in a vacuum	1.09	0.23	0.007	0.011	0.27	Bur. Mines	0.007	0.044	0.010	0.007

[a] Analysis of residue. [b] HCl method.

modification of this method or an entirely new procedure may be proved to be superior, but if MnO, MnS, FeS, SiO_2 and Al_2O_3 are to be determined in plain carbon steels, this method will be found to be entirely satisfactory and so superior to previously published methods that it is hoped it will become a standard procedure. No attempt has been made in this paper to substantiate the method, but another publication[7] which will appear in the near future will contain considerable confirmatory evidence

DISCUSSION

(F N Speller presiding)

F N SPELLER, Pittsburgh, Pa —The procedure described in this paper is looked upon as one of the real accomplishments of this cooperative work during the past five years

A B KINZEL, New York, N Y (written discussion) —The problem of the determination of inclusion content of steel has long been of interest to us at the Union Carbide and Carbon Research Laboratories, and we were particularly pleased to see this detailed description of the method used at the Bureau of Mines   The paper has been reviewed by Messrs Cunningham and Price, analytical chemists, as well as by Mr Crafts and the writer, and this discussion embodies our joint ideas on the subject

The importance of this subject cannot be overemphasized, as the knowledge of inclusion content of steels is essential to a better understanding of the whole problem of the characteristics of steelmaking and the physical properties of the steel, and we are certainly indebted to Dr Fitterer for his thorough investigation of the possibilities of electrolytic extraction   The work is brilliantly conceived, and while we object to many of the conclusions drawn, we believe the experimentation has been well worth while and that further study may overcome some of these objections

It is greatly to be regretted that the method is limited to the type of inclusions mentioned in the title of the paper, particularly in view of the fact that it is highly probable that the iron oxide content alone is fully as important as all the rest of the oxides in the steel, if not more so   This is true not only as the iron oxide content itself affects the properties of the metal, but also as the iron oxide is intimately associated with the other oxides in the inclusion formation, so that type and character of the inclusions which contain MnO and SiO_2 are profoundly influenced by the iron oxide content   Thus, even if we have a satisfactory method for the determination of Mn and Si oxide content, we would probably be in a very poor position to effect correlation between this oxide content and the physical properties of the steel

Interrelation of inclusion constituents as they affect the inclusion content—commonly known as cleanliness of the steel—is generally recognized   Not only is the iron oxide an important factor in determining the type of inclusions which may result with a given MnO and SiO_2 content, but also it has been shown that the sulfur content is extremely important, and that the relative proportions of sulfur and oxygen in inclusions are probably much more important than the absolute amount of each, which can be found by analysis of the steel   This is well illustrated by values given by Benedict and Lofquist, as well as by the curve in a paper on inclusions in this volume (p 143).

It is unfortunate that Dr. Fitterer did not see fit to give some justification of the method along with the detailed procedure   In view of this, it may not be pertinen

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[7] Reference of footnote 1

to give a critical discussion of the method   However, as this seems to be the only opportunity, we feel that the following comments are in order   Ferrous and ferric hydroxide, according to the author, contaminate the inclusion residue   This phenomenon of course, is caused by hydrolysis in the neutral solution   It is well known that manganese hydrolyzes in a neutral solution in the presence of ferric hydroxide or on exposure to air   Thus, from the analytical standpoint, it seems highly probable that some of the manganese entering the solution does hydrolyze   This would then be found in the residue and reported as manganese in inclusions rather than manganese in solid solution in the steel   Work at these laboratories, using low-carbon material with varying manganese contents, showed this hydrolysis to proceed partly as a function of the manganese content   Thus, with manganese less than 1 per cent, the effect is much less than with much higher manganese content, nevertheless it is present, so that there seems to be little doubt that at least some of the manganese reported as MnO comes from the steel proper

In the procedure the sample is not entirely dissolved   Thus, we encounter selective corrosion in locations having higher inclusion content than others   In extreme cases, this results in a residual ingot which looks like a piece of wood full of wormholes   In less extreme cases, the ingot may appear to be fairly uniformly attacked, but even in this case portions higher in inclusion content have been more readily attacked, and the resultant inclusion figure always tends to be high   We believe that it is essential in any accurate analytical method for inclusions in steel, that the entire sample be completely dissolved   The use of a sample which is only partly dissolved leads to further difficulties due to the sticking of the residue to the sample, and we note that the author resorts to a rubber "policeman" to scrape the residue from the sample   This involves another probable error   Small particles of the metal may well be left on the surface owing to selective attack caused by microsegregation, which we know to be present in all steels   These particles then will be scraped down into the nonmetallic residue along with the nonmetallics which adhere to the surface, and this error would be far from constant with different steels or even with the same steels and different casting practice

The methods used for analyzing the residue after the extraction also deserve comment   The sodium hydroxide method for the determination of alumina is very difficult to carry out in the presence of a preponderant amount of iron such as exists in this case   Thus, instead of a single sodium hydroxide separation and a single ammonia separation, at least two such separations should be resorted to   Moreover, a blank determination using an equivalent amount of reagents should also be run   Dr Fitterer agrees that the best procedure for determining relatively high alumina is the hydrochloric acid extraction on a large sample, and our experience indicates that it is equally satisfactory for low alumina   However, even with this procedure careful residue analysis is necessary, as we have found considerable iron oxide with the alumina

When analyzing the filtrates, designated as A and B by the author, it is not at all probable that the chlorides are removed by the methods described   Retention of these chlorides would result in an apparently low manganese result   Moreover, when working with filtrate B, we cannot hope to determine the true manganese content because some of the manganese will always be held with the iron-aluminum hydroxides in the alumina determination   Regarding the separation of the oxides and sulfides, we would note that the manganese oxide is soluble in 50 per cent electrolyte and sodium citrate solution   It seems to us much more probable that this apparent MnO solubility is really a solution of the hydrated oxides resulting from the hydrolysis during the electrolysis   Furthermore, in connection with the MnO-MnS separation and the FeS determination, it is highly probable that during the electrolysis some of the sulfides are dissociated, leaving sulfur as such in the residue   In order to check this,

a number of samples of steel containing from 0 10 to 0 50 per cent carbon, 0 40 to 1 20 per cent manganese, and 0 025 to 0 050 per cent sulfur were analyzed by the electrolytic method, as described in this paper   The inclusion residue was treated with concentrated hydrochloric acid in an all-glass Pulsifer flask, and in no case was more than 25 per cent of the total sulfur content in the steel found by this extraction Most of the analysis showed only 10 per cent of the total sulfur   Thus, the remaining sulfur must be present as elemental sulfur, which means that in the electrolytic extraction the sulfides are dissociated   If all the FeS and MnS in the steel are found in the inclusion residue, all of the sulfur in the steel should be evolved on the boiling hydrochloric acid treatment

In the above discussion it seems to us that the method is wanting, first, in that iron oxide is not determined, second, in that MnO and MnS must be reported together, and even then the results of the total are open to serious question   The methods of analyzing these constituents seem to be unsatisfactory   The method for alumina is difficult, and could well be supplanted, as the author suggests, by the hydrochloric acid method   The silica analysis seems to be satisfactory   Here again, less difficulty is encountered with other methods   Thus, while we feel that Dr Fitterer has done work which was well warranted and which has increased our knowledge of the art, and that our appreciation and compliments are due him, we believe that much more work on the method is necessary before it can be accepted as a satisfactory analytical method

O V GREENE, West Reading, Pa (written discussion) —The development of a satisfactory method for the determination of the nonmetallic inclusions in steel is of the utmost importance   Without some method to determine the amounts and character of such inclusions, the steelmaker is at loss to determine either the quality of his product or make improvements   The microscope has been employed both qualitatively and quantitatively for this purpose, but this method is not particularly satisfactory, because it is very tedious, and at best only a small portion of the specimen will be examined   It has been shown further that the chemical methods used previously have invariably attacked the inclusions   Electrolytic extraction, on the other hand, is not only productive of a more representative sample, but the mineralogical characteristics of the inclusions may be determined accurately

Dr Fitterer and his coworkers are to be congratulated on the development of a method for electrolytic separation   Since the academic side of this problem has been more or less solved, we hope that the extensive program undertaken by the Bureau of Mines in conjunction with the Carnegie Institute of Technology and the Metallurgical Advisory Board can be continued further   The practical application of such methods is extremely vital   The significance of various amounts, types and segregations of nonmetallic matter on the resultant properties of steels should be definitely established It may be good economy, for instance, to use a steel containing 0 05 per cent inclusions for certain types of work, while other applications may require inclusions under 0 01 per cent

We have successfully extracted nonmetallic inclusions electrolytically on a number of low-carbon, low-alloy steels   As Dr Fitterer points out, there is considerable contamination of sludges from alloy steels, particularly when chromium is present The chromium carbides apparently do not dissociate during the electrolysis, and remain in the sludge as such   However, the chromium is ignored much the same as the iron, as described in the present paper, and since the steels we have been working with contain only small amounts of carbon, no detrimental influence has been observed

The ferrous and ferric hydroxides and basic ferrous sulfates have been reduced to a minimum or entirely eliminated by the use of electrolytes slightly different from those employed by Dr Fitterer.   The sols we are using were developed by Dr Styri who, I believe, is to describe them shortly

In a memorandum from the Bureau of Mines of Jan 7, 1931, it is stated that neither sodium nor ammonium citrate can be used as a buffer solution, since these materials attack MnO   However, in the steels we have investigated there is no free MnO   Furthermore it has been established that the sodium citrate used in the fashion to be described by Dr Styri does not attack the manganese-silica-alumina compounds which are predominant in our product, which is basic electric steel   The formation of the ferric hydroxide is further prevented by covering the whole electrolyte bath with a layer of petrolatum, which excludes the air   We have never been successful in the use of collodion bags because they became brittle and could not be handled successfully   At present we are employing cellophane bottle caps furnished by the E I du Pont de Nemours Co , which are approximately 55 mm in diameter and 110 mm deep   This type of bag necessitates the use of a No 10 rubber stopper which loosely fills the top of the bag   This material is extremely strong and tough, and may be handled almost as though it were a glass beaker   It may be cleaned by a policeman and washed with a stream from a wash bottle   While the walls of these bags are considerably heavier than those obtained with collodion, the capillaries are large enough to permit the free migration of the iron ions, consequently anodic consumption of approximately 1 gram per hour is obtained

Our current density and voltage are the same as those employed by Dr Fitterei We have found that it is not necessary to use platinum wires to suspend the anodes Lead wires $\frac{1}{8}$-in dia threaded at the end are screwed into tapped holes in the anodes The top of the anode and the exposed portion of the wires are coated with candelilla wax   We are also indebted to Dr Styri for suggesting the use of the petrolatum cover on the bath, the cellophane bottle caps and candelilla wax

We have found that the sludges were not only contaminated with carbides, but with bits of anodic material that were mechanically separated   During the electrolysis of certain types of steels, the specimens became honeycombed and a considerable amount of metallic material was undermined and disengaged, which accumulated in the sludge Dr Fitterer does not record such conditions, which possibly may be peculiar to the types of steels we have investigated   Various methods for the separation of this metallic matter have been tried, but only one has been successful   Magnetic separation, centrifuging and flotation were not satisfactory   A chemical method used by the Union Carbide and Carbon Research Laboratories, which employs a ferric iodide solution of iodine, has proved satisfactory for the elimination of this metallic matter Our sludges as they come from the bags are filtered off, washed and dried, and then exposed to the action of the ferric iodide solution   From this point our method of analysis is entirely similar to the one outlined in Dr Fitterer's paper

Table 2 shows a few of the results we have obtained on various steels

TABLE 2 —*Tests by Carpenter Steel Company*

S A E No	Type Analysis, Per Cent				Electrolytic Extraction, Per Cent			
	C	Mn	Cr	Ni	SiO_2	Al_2O_3	MnO	Total
3312	Max 0 17	0 30–0 60	1 25–1 75	3 25–3 75	0 0053	0 0166	0 0018	0 0237
3312					0 0030	0 0171	0 0008	0 0209
3312					0 0044	0 0164	0 0039	0 0247
3312					0 0048	0 0122	0 0007	0 0177
3120	0 15–0 25	0 30–0 60	0 45–0 75	1 00–1 50	0 0121	0 0060	0 0015	0 0196
3120					0 0107	0 0038	0 0020	0 0165
3120					0 0095	0 0033	0 0072	0 0200
2512	Max 0 17	0 30–0 60		4 75–5 25	0 0119	0 0030	0 0008	0 0157

F W Scott, Indiana Harbor, Ind (written discussion) —My work has been almost exclusively confined to basic open-hearth steel of the following composition 0 60 to 0 90 per cent carbon, 0 60 to 0 90 per cent manganese, less than 0 040 per cent phosphorus, less than 0 040 per cent sulfur, and 0 150 to 0 250 per cent silicon   These steels were deoxidized with spiegel and ferromanganese in the furnace, and ferromanganese and ferrosilicon in the ladle   The following difficulties were so often encountered that we were forced to use other methods for the determination of the manganese-silicate inclusions

The main difficulty encountered was the presence of undecomposed iron or steel in the residue   The amount of the metallic particles found in the residue varied widely, 0 16 to 2 43 grams, but in sufficient amount to cause the results to be worthless   An examination of the sample after the removal from the collodion bag brought out an interesting fact   The carbon residue near the surface of the steel was different from the outside of the "shell "   It was ' grayish" and adhered rather tightly to the specimen   On the hands it had the appearance of graphite   This apparently was where most of the metallic contamination occurred for when the sample was scraped with a rubber policeman and washed off, this carbon with the metallic particles was added to the residue   Another indication of the metallic particles was that the entire residue appeared to be magnetic.

A second trouble was the presence of a small amount of silicic acid in the residue Careful study showed that it occurred in some amount in almost all extractions of silicon-treated steels, and the longer the cell operated the larger was the percentage of the silicic acid   Samples of 55 and 60 grams were extracted and the residue found to contain large amounts of contamination

We had no trouble with the mechanical operation of the extraction, but are convinced that the contamination is too great for the results to be reliable   We agree that high-manganese and high-silicon steels (1 50 per cent Mn and 0 20 per cent Si) are not applicable to this extraction, as we found the same trouble in these as in the ordinary carbon rail steels we have described

I hope that Mr Fitterer may be able to suggest the cause of the trouble we have encountered, but we find his method to be unsuitable for silicon-killed, high-carbon steels

We have developed an electrolytic method in our laboratory which we have found to be suitable for the extraction of MnO and SiO_2 from all carbon steels   This method will be published in the near future, and offers many improvements on the older well-known methods

H Styri, Philadelphia, Pa —I do not think we have gone far enough in our experiments to give definite results   Perhaps I belong to the old school, where it was taught that we should not present anything until we had real results, but I am afraid that development along that line will go too slowly, and I think the present method of giving progress reports may be advantageous   So I am going to follow that suggestion and give our experience

We have been working on inclusions for eight or nine years   At first we tried out chemical methods and did not get much encouragement   We had some fair results but nothing satisfactory   The only definite point was that the electrolytic method seemed to be the only solution   Trying that again we were stumped   We did not think of the method of using collodion membranes and we were very glad when we learned about it from the Bureau of Mines   The method is an old one used in electrolytic processes, but something always slips one's mind

When we heard about this method from the Bureau of Mines, we began to look for a suitable material and fortunately got in touch with the du Ponts, who gave us the bottle caps mentioned by Mr Greene to experiment with   They were very good   We used the solutions as recommended by the Pittsburgh Experiment Station

and we had some fairly good results, but we also had considerable difficulty, for several reasons

We discovered later that one of the reasons was that the chemical we used was not pure We used a ferrosulfate that was slightly oxidized, that caused trouble in the electrolysis because it formed sludges on the bag Trying to eliminate these causes, we adopted the different means that Mr Greene has referred to of protecting the surface of the bath with a thin layer of paraffin The paraffin at 100° F melting point is melted and poured over the bath, when it solidifies An 8-in layer or less will protect from oxidation

The principal point we were after was to get 100 per cent recovery of the sulfides, because our theory was that if we could recover the sulfides, we would also be able to recover most or all of the other inclusions When we used the Bureau of Mines method, we could not get complete recovery of the sulfides, and we suspected that we had some acid attack Consequently we used another trick applied in electrolysis in order to keep the liquid inside the bag slightly alkaline We used an electrode of lead protected with candelilla wax, as described by Mr Greene

Inside the bag we use a solution of 10 per cent sodium citrate Outside we use 3 per cent solution of ferrous sulfate, but in addition to that we have 0 1 per cent H_2SO_4 The reason for that slight acidity is that we want, if any hydroxide should form, to prevent it from forming sludge on the bag by keeping it in slightly acid solution With these solutions the paraffin layer is not necessary

Theoretically, if it were 100 per cent current efficient the alkaline inside the bag should be constant, but as it is not 100 per cent efficient, the solution inside becomes less alkaline or slightly more acid

That is not so dangerous if you do not complete the solution of the sample and stop, as the Bureau of Mines does, but we had the same objection to the method as mentioned by Mr Kinzel—that we do not get everything in the sample in solution We wanted to take the whole sample into solution So by getting down to the last piece of the material there is more tendency to get acidification inside By using a 10 per cent sodium citrate inside the bag we can completely dissolve the sample, weighing about 30g, and still have alkaline solution We get 100 per cent recovery of the sulfides Of course other combinations of electrolytes readily suggest themselves

Most of our tests have been on high-carbon steels and alloy steels

The difficulty is to analyze the residues, and separate the sulfides or silicates from the carbides We have not been able to get rid of the carbides, and I have questioned that Dr Fitterer has proved that he is entirely rid of the carbide In order to conserve time I will not go into this any further Just in this I believe we have the present greatest difficulty—to get that separation of carbides from the silicates and the sulfides We are working on that at the present time Unfortunately, we cannot do anything more than spare-time work on it, but we believe that we can at least dissolve the silica in the silicates without disturbing the carbides and we can determine the amount of sulfide

I question one thing in Dr Fitterer's paper He says he gets 100 per cent recovery of the sulfide, but in Table 1 take the first three samples showing 0 03 per cent sulfur The recovery of manganese oxide plus manganese sulfide is no more than 0 03 That means that the MnO + MnS is no more than the original sulfur Of course, it may be possible that he had some iron sulfide, but where is it? I should like to have some more definite proof that this residue contains the total amount of sulfur and no carbides

G R FITTERER (written discussion*)—I regret that some of the discussers did not give a complete description of their experiments and results Because they

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neglected to do this, they have unknowingly made it difficult for me to answer some of their remarks

It is rather unfortunate that we felt inclined about a year ago to distribute an advance notice of our electrolytic process   At that time we were uncertain as to the applicability of the method   However, there was a great demand for such a procedure and a very brief description of the method was written for immediate release   Consequently, the method has been misapplied in many instances and I feel certain that some of the remarks made by the discussers have been based on the hasty application of the method described in the advance report and not upon the method (together with its many precautions) which was described in my paper   Hence I beg of those who have conscientiously attempted to apply this method (as described a year ago) and who have encountered difficulty, to reconsider the method in the light of the additional information given today

Some of the discussers have certain common objections to the method which I have just described   For example, Messrs   Greene, Kinzel, Scott and Styri all mention the presence of large amounts of metallic iron and undecomposed carbides   Mr   Scott says that the metallic iron in his residues often reaches 2 grams   If this is the case, he is not operating the method as recommended in this paper   Our metallic contamination seldom exceeds 0 01 to 0 02 g   The operator will find that careful observance of precautions 4, 5 and 9 (p 206) will eliminate practically all of the metallic iron

Since giving this paper I have reviewed some 50 analyses of residues and have found that in no case did our total residue after ignition weigh more than 0 3 g   Let us suppose as an extreme case that all of this residue is metallic iron containing 1 per cent Mn and 0 1 per cent Si, and that an average of 30 g of steel was dissolved in each case   The manganese contamination resulting from 0 3 g of metallic iron is equivalent only to 0 0129 per cent MnO in the steel   It is obvious that all of this residue (0 3 g) is not metallic iron, hence this is an extreme test   The SiO_2 equivalent of contamination resulting from the same metallic residue would only represent

$$\frac{0\ 3\ (gram\ metallic\ iron) \times 0\ 1\ per\ cent\ (Si\ in\ steel)}{30\ grams\ steel\ electrolyzed} \times \frac{60 \times 100}{28} = 0\ 0022\ per\ cent\ SiO_2$$

This is within the experimental error of the method, therefore I feel that on this point the discussers are worrying about trifles

Mr   Greene and Dr   Styri are discussing the electrolysis of low-alloy steels, for which the method described in my paper is not recommended   In this case I feel certain that the greatest amount of their metallic material is really undecomposed chromium carbide (possibly combined with some manganese and iron carbides)   Hence the residue cannot be accurately analyzed for MnO and Cr_2O_3 We have been able to partly decompose chromium carbides by evacuating the residue in the presence of some of the electrolyte but are not at all certain that they are completely decomposed   This decomposition *in vacuo* is effected by means of reactions involving the formation of hydrocarbons   The hydrocarbons are drawn off, thus continuing until practically all of the carbides have decomposed

I would not recommend the ferric iodide solution of iodine for the elimination of carbides or metallic iron from the residue in samples on which MnO is to be determined   This solution dissolves MnO to a great extent, as it does some of the manganese silicates   I am convinced that some loss of silica (in manganese silicate) is encountered through the solubility of manganese silicates in this solution   However, Mr   Greene's steels contain very little if any manganese silicates and therefore I believe that his results are reliable

Dr   Styri questions whether we were able to thoroughly decompose the carbides, and by talking with him I find that he was speaking of low-alloy steels (containing about 1 per cent chromium)   The method is not recommended for steels of this

t\ pe and I hope that this point is thoroughly understood by everyone trying to apply this method to their materials   Further work must be done before all of the inclusion materials can be satisfactorily determined in steels containing carbide-forming alloys

We have proved to our own satisfaction that Mn_3C and Fe_3C do not contaminate the inclusion residue   Our procedure in this connection was to electrolyze ferromanganese containing 80 per cent Mn and 8 8 per cent C   This material certainly is composed entirely of Fe_3C and Mn_3C, yet upon electrolysis of 30 g of ferromanganese only 0 3 g of manganese was obtained in the residue   In other words, about 24 g of manganese (as Mn_3C) was electrolyzed and only 1 per cent contaminated the inclusion residue

According to Arnold and Read[8] a steel containing 0 40 per cent C and 0 60 per cent Mn contains 0 20 per cent Mn in the carbide   If 30 g of this steel were electrolyzed and none of the Mn_3C decomposed, the residue would contain 0 20 per cent times 30 or 0 06 g Mn   But by analogy to the ferromanganese electrolysis and manganese contamination only 1 per cent of this would be present in the residue, because 99 per cent of the Mn_3C has decomposed on being exposed to the electrolyte   Hence 1 per cent $\times$ 0 200 per cent = 0 002 per cent Mn contamination would exist, or, in other words, 1 per cent $\times$ 0 06 g = 0 0006 g Mn (as Mn_3C) contaminates the residue

The above, of course, is an extreme test because the 1 per cent contamination mentioned above may be due to other factors   We have made other experiments which are more convincing than that described above but they are too lengthy to give here

Dr Styri and Dr Kinzel feel certain that the method which I have proposed does not extract all of the sulfides   Their experiments were conducted by dropping HCl into a flask containing the inclusion residue and collecting the H_2S formed in the usual manner   These experiments could not be expected to give accurate results and were not conducted as were ours   It is highly essential that zinc be placed in the flask and that the acid be added slowly   Hence both H_2S and H_2 gases will be formed   The H_2 acts as a carrier gas for the H_2S and in this manner all of the sulfide sulfur is found in the residue   For example, we electrolyzed a steel containing 0 077 per cent S and obtained a value of exactly 0 077 per cent S (on the basis of steel electrolyzed) in the inclusion residue by conducting the experiment in the above manner   A blank was run on the zinc and filter paper and found to be negligible   It was also found to be essential that the residue on the filter paper shall not dry out   The evolution takes about one-half hour

I have had no experience with the sulfides in low-alloy steels

Some of the discussers have expressed a desire to electrolyze the entire sample and have made certain alterations in the electrolyte and the mounting of the sample so as to accomplish the complete solution   The experimental error in stopping electrolysis after 20 to 30 g of metal has been dissolved is a very small value (less than 1 per cent)   The advantage gained in accomplishing this factor introduces other errors which are more detrimental than in the opposite case   Hence the remedy is worse than the disease

When citrate and sulfuric acid are added to the electrolyte the solubilities of the inclusions are greatly increased   Also, as the sample becomes very small the current density is so great that anodic reactions occur which increase the solubilities

With particular reference to Mr Greene's discussion, may I point out again that the method described in my paper is recommended only for plain carbon steels   Mr Greene and his associates have made a distinct contribution to this subject in their attempt to apply the procedure to the determination of only Al_2O_3 and SiO_2 in low-alloy (particularly chromium) steels   Hence anyone using their modification must

[8] J O Arnold and A A Read   Chemical and Mechanical Relations of Iron, Manganese, and Carbon   *Jnl* Iron and Steel Inst. (1910) **81,** 169–179

keep in mind that their procedure cannot be used for the determination of MnO in any class of steels because of the changes made in the electrolyte   All of the MnO and part of the MnS will be dissolved by this solution

The cellophane bottle caps described by Mr Greene will unquestionably be a great aid to operators who have never been satisfied with the collodion bags, which had to be prepared by hand   We made certain tests on these bags after we learned of them from Mr Greene and found that they were quite as satisfactory as those prepared from collodion   I would like to insert a word of caution at this point, however, and point out that these bags cannot be used more than once in the ferrous sulfate-sodium chloride electrolvte, inasmuch as the hydroxides fill up the pores and render them impervious to the various ion complexes   If only determinations of Al_2O_3 and SiO_2 are to be made on the residue (as is done at the Carpenter Steel Co), the citrate solution can be used, the formation of hydroxides will be inhibited, and the bags may be used several times

I am sorry that Dr Kinzel considers the method highly inadequate in all respects I feel that the reason for this is that he and his associates have not visited our laboratories with the intention of determining exactly how our cells operate and how our analyses are made   I am sorry that they have neglected to do this, because in every case where trouble has been encountered and a visit has been paid us by other laboratory workers, the operators have discovered some fault in their application of the method   An open invitation was issued about a year ago to all those interested, and I wish to give a specific invitation to Dr Kinzel and his associates to visit our laboratories for a day or so to study our procedure in operation, so that a comparison can be made with their application of the electrolytic procedure

I do not agree with Dr Kinzel that ferrous oxide is more important than all of the other oxides   More than 50 per cent of the steel manufactured in this country is "dead" killed or completely deoxidized   In these steels the FeO content is negligible Of the remainder some 20 per cent is semikilled, and 30 per cent is rimming steel Hence I will admit that FeO is one of the most important oxides in 30 per cent of the steel made in this country   However, even in this material manganese oxide is just as important a factor as is ferrous oxide

In the first paragraph on the fourth page of my paper I have pointed out that FeO is entirely insoluble in the electrolyte and that a new method is being devised which will quantitatively determine this material   When this work is completed a thorough study of the oxides in rimming and semikilled steels may be made

I do not believe that Mr Kinzel has any point to prove concerning the ratio of oxides to sulfides as given in his paper on inclusions (page 143 of this volume)   In the first place, I believe that anyone who uses that method of inclusion counting is wasting his time   In the second place, the oxide data were obtained by Cunningham's iodine extraction method   We received a copy of Cunningham's method two years ago and although it is practically identical with that of Westcott, Eckert and Einert, we subjected it to a fair series of tests   We found that it was totally unreliable, for various reasons, and continued with our development of the electrolytic method I wish Dr Kinzel would explain the significance of the figure to which he has referred (Fig 19, p 169)   As yet neither he nor anyone else has sufficiently explained this plot

Dr Kinzel says that manganese hydrolyzes in the electrolyte and cites certain experiments made at his laboratories which confirm this point   If these experiments were particularly conclusive, the results should have been included in his discussion

I feel that the experiments which I described in my paper were quite conclusive in showing that $Mn(OH)_2$ does not form from the electrolysis of the element manganese which is alloyed with iron   For example, manganese-free electrolytic iron was melted and thoroughly deoxidized with aluminum; then 0 66 per cent manganese was added   Although no MnO should form under these conditions, some MnS

could be expected because the metal contained from 0.01 to 0.02 per cent S. This was found to be the case because 0.022 per cent MnO (+MnS) was reported, which was later found to be entirely MnS by the citrate separation. Hence no MnO was found and no Mn(OH)₂ had formed during electrolysis, since no citrate-soluble material was obtained. Had some Mn(OH)₂ been present, it would have been soluble in citrate and reported as MnO.

Dr. Kinzel says that "the apparent MnO solubility in citrate solutions is really a solution of the hydrated oxides resulting from hydrolysis during electrolysis." We would not state that MnO is soluble in this solution without having first made some actual tests on MnO. This solubility was determined on samples of pure MnO and not on the regular inclusion residue. Hence no assumption was made in determining this point. On page 205 I have pointed out that MnO is soluble and MnS insoluble in citrate solution. Hence Dr. Kinzel's point in this regard is rather weak.
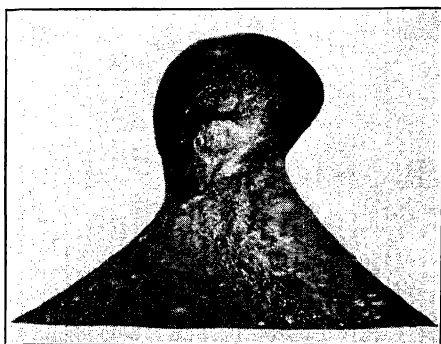
FIG. 3.—PARTLY EXTRACTED MANGANESE SILICATE INCLUSION.
Reduced one-tenth. Original magnification 400.

Dr. Kinzel's statement that "selective corrosion in the localities of high inclusion content causes 'wormholes' to appear in the surface of the sample" is directly contradictory to our experience. Instead, the inclusions inhibit the electrolysis of the metal beneath them and in the end are represented by little mounds, each of which is topped by an inclusion. Fig. 3 illustrates this point. This is a very large inclusion but the same phenomenon occurs even in the case of very small particles. Ordinarily this effect is microscopic. Hence it is not essential to completely dissolve the electrolytic sample. If the sample is as large as specified in the paper and 20 to 30 g. of steel is dissolved, the analytical error will be negligible.

I believe that a good analyst will experience no decided difficulty in making the alumina separation, although I will agree with Dr. Kinzel that it is advisable to make a double separation. We have definitely determined, however, that well over 90 per cent of the alumina is separated by the first treatment. In discussion of this point, Dr. Kinzel says that the hydrochloric acid method is satisfactory for steels containing small amounts of alumina. This is in direct contradiction to our findings, inasmuch as we have definitely determined that in low-alumina steels, iron and manganese aluminates or aluminum silicates exist. All of these have appreciable solubilities in hydrochloric acid.

No good analyst should experience any difficulty in using the bismuthate method for manganese and in this connection I am certain that the presence of chlorides is easily determined.

I am interested to learn that Mr. Scott has devised an electrolytic method which is entirely suitable for the extraction of MnO and SiO₂ from all carbon steels. If

this is the method I had the privilege of reviewing, I am certain that it will never be useful for MnO or manganese silicates because these materials are soluble in the electrolyte   It may be ideal for steels such as Mr Greene is studying, which contain only SiO₂ and Al₂O₃   The method has its good points but I am afraid it operates at too high an acidity for the accurate extraction of many inclusions   Certain changes may have been made since I read this manuscript, and for this reason I offer Mr Scott my best wishes and I hope that he has devised a better method than that described herein   I have stated in my paper that it is my hope that this publication will stimulate interest which will culminate in developments of newer and better methods

Dr Styri should be highly commended in his attempt to apply this procedure to his special types of steels   I only wish that our program were extended to include the electrolytic extraction of inclusions from alloy steels   However, since this is not the case, I wish him luck and hope that some of his experiments will later be made available to the public

I have already answered some of the particular points which Dr Styri has brought up, namely, the solution of the entire sample, the falling metallic particles, the contamination resulting from the presence of carbides in the residue, and, finally, the determination of sulfide sulfur in the residue

Dr Styri is particularly interested in the sulfides and states that the 0 03 per cent S in the first three samples listed in Table 1 was not recovered because the MnO + MnS value is no greater than 0 03 per cent   This is not a strong argument because no determination of FeS was made in these steels   FeS does not influence the determination of MnS   The only way to determine the amount of sulfide sulfur is to run an evolution analysis using zinc (as described above)

I have been encouraged rather than discouraged by the discussions because no point was raised concerning the extraction of inclusions from plain carbon steels which could not be readily answered from experiments which we have already made   May I suggest that a final decision on the applicability of this method be withheld until the Bureau of Mines report of investigations has been published   All of the confirmatory data necessary to answer the questions raised today will be given therein

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The Permanent Growth of Gray Cast Iron[*]

By Walter E. Remmers,[†] Chicago, Ill.

The fact that gray iron increases in volume, cracks and distorts upon repeated heating and cooling is rather common knowledge. In ingot molds, Diesel engine pistons, carburizing boxes, continuous furnace parts, grate bars, stoker parts, and all castings that are subjected repeatedly to high and low temperatures, the phenomenon of growth presents a vital problem. Ingot molds distort and produce cracks which result in seams or laps and later appear as defects in the finished product. The heads of Diesel pistons frequently fail by cracking in a stellar shape. This is attributed usually to the result of permanent growth. Distortion and change of dimension of furnace parts frequently renders them entirely unusable. In chain grate stokers, mechanical difficulties frequently are caused by the growth of the links. In proper operation these links should never attain a temperature sufficiently high to start growth, nevertheless, some have grown ⅛ in. on an 8-in. length when improperly operated. Even though the phenomenon is generally known there still exists a deficiency in the explanation of the mechanism of this growth. The field of investigators of this subject has a decided variation in opinion concerning the causes. The problem is of sufficient importance therefore to warrant further consideration.

Review of Published Work

Since the published work, particularly the European, contains much detail, only the outstanding results and conclusions of the investigators will be reviewed.

The pioneering investigations of Outerbridge in 1904 and 1905 brought forth the conclusion that growth was not a function of chemical or crystallographic changes but was a result of the formation of fine hair cracks. These cracks are supposedly due to a nonuniformity of thermal expansion and contraction which ruptures the structure of the material. More recently Benedicks and Lofquist presented a purely mechanical theory, which is similar to that of Outerbridge. These investigators believe the temperature gradient from the outside to the center of the cast piece causes a contraction of the outer layers on passing

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through the A_1 transformation, while the interior of the cast piece has not yet reached the temperature necessary for the change   The effected stress set up between the outer and the interior layers causes the numerous fissures in the material   Outerbridge also believes that the increased pressure of occluded gases at higher temperatures plays an important part in the process of growth   In this latter statement Outerbridge is supported somewhat by Okochi and Sato, who accept, as the main cause of growth, a trapping of penetrated gases by a decrease in the porosity of gray iron which they believed accompanied an increase in temperature

In direct contrast to these opinions are the conclusions of another group of investigators Rugan and Carpenter, Andrews and others, who agree in the main, if not in detail, that growth is caused by oxidation of the graphite flakes by the surrounding air, the penetration of air along these voids resulting in the oxidation of the silico-iron matrix   Since the increased volume of the oxide is greater than the volume evacuated by the graphite flakes, an internal growth forces the matrix apart into more space

Later tests by Taria Kikuta show by experimental proof that the assertion of the aforementioned scientists with regard to the penetration of gases does not coincide with the facts   Porosity increases with repeated heatings and at high temperatures the gas penetration through gray cast iron is only slightly less than at room temperature   Kikuta takes the stand that as a result of his tests neither the expansion of occluded gases nor the oxidation alone can produce the obtained volume increase

Practically all of the investigators agree that the relatively large initial growth is a result of decomposition of the cementite which may either be eutectoid, hypereutectoid or eutectic, depending on the degree of grayness of the iron

Oberhoffer, Piwowarsky and many others have carried on extensive research upon the effect of the various impurities, as well as alloy additions upon the irreversible growth phenomenon   Piwowarsky and Esser have collected all of this work into a comprehensive report which was published recently

PRESENT INVESTIGATION

The writer has reviewed the literature and has selected a series of experiments, the results of which might serve to coordinate the diversified conclusions and establish an explanation which is applicable to all cases of growth of gray iron

In 1926 Meinholtz, under the direction of the writer, carried on a number of experiments in order to determine the effects of repeated heatings in a medium free from oxygen and to study the effects of prolonged heatings at various temperatures   Later the writer selected

various determinations needed to fill in some of the gaps.   As a result, several experiments were made that would serve to unify some of the previously existing data.

Three series of heats were made on test bars cast from the same ladle of commercial cast iron.   In these experiments all conditions were the same with the exception of the cooling rate.   One series was permitted to cool in the furnace, another at an "air rate," and a third was given an oil quench.   In the air rate the sample was protected from oxidation by permitting it to cool in a light sheet-iron can.   The pieces were heated in a gas-fired furnace with the test bar inclosed in a sealed cast-iron box, Fig. 1.   A typical analysis of the furnace atmosphere is as follows:
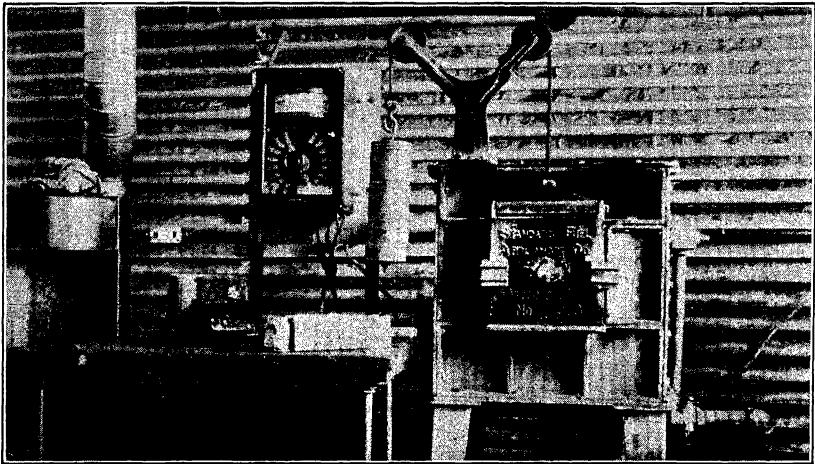
FIG. 1.—FURNACE AND ACCESSORIES USED IN FIRST PART OF WORK.

CO_2, 13.4 per cent.; O_2, 0.6; CO, 0.4.   Such a gas permitted a slight amount of oxidation.   The quenching oil was a light mineral oil with a low viscosity, in order to secure a rapid cooling for purpose of contrast.

The original test bars were of the following analysis: Total carbon, 3.32 per cent.; combined carbon, 0.20; graphite, 3.12; phosphorus, 0.69; sulfur, 0.073; manganese, 0.46; silicon, 2.63.   This iron was used because it was known that a decided growth would result.   In all later experiments test bars cast from this same ladle of metal were used.

The actual growth of these three bars after 25 repeated heatings to 900° C. (1652° F.) and holding for 1½ hr. is: furnace cool, 42.19 per cent. increase in volume; oil quench, 35.87 per cent.; air cool, 37.02 per cent.

Fig. 2 indicates the rate of growth, which seems to indicate that ultimately a constant volume is approached.   Fig. 3 shows the

test bars upon completion of the experiments   Fig 4 shows a section
of the original specimen in the unetched condition at 200 dia and Fig
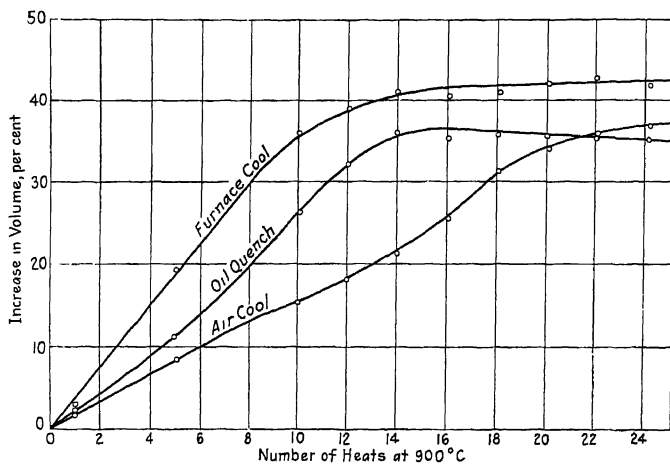
FIG 2 —INCREASE IN VOLUME
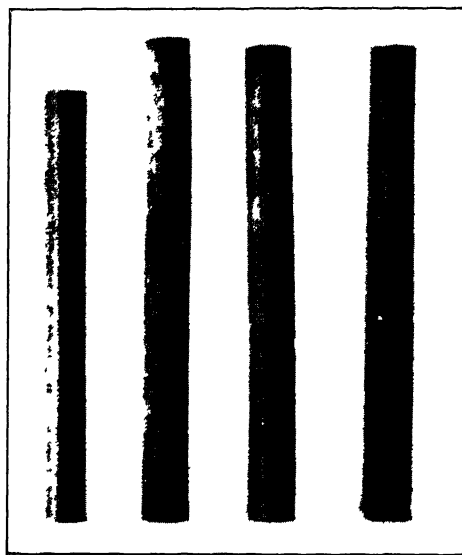
FIG 3 —TEST BARS BEFORE AND AFTER GROWTH

1 Original bar   3 After air cool
2 After furnace coolings   4 After oil quench

5 the same piece in the etched condition, the combined carbon appearing
in pearlite as the dark areas not shown on the unetched sample   Figs
6, 7 and 8 represent the conditions in the unetched pieces after exposure

to repeated heatings and coolings. What formerly appeared as graphite flakes now has the appearance of a voluminous and ragged network of voids and graphite, the structure from the slower cools being slightly coarser. The resulting difference in structures is probably caused by a difference in the time element necessary for the coalescence of the carbon
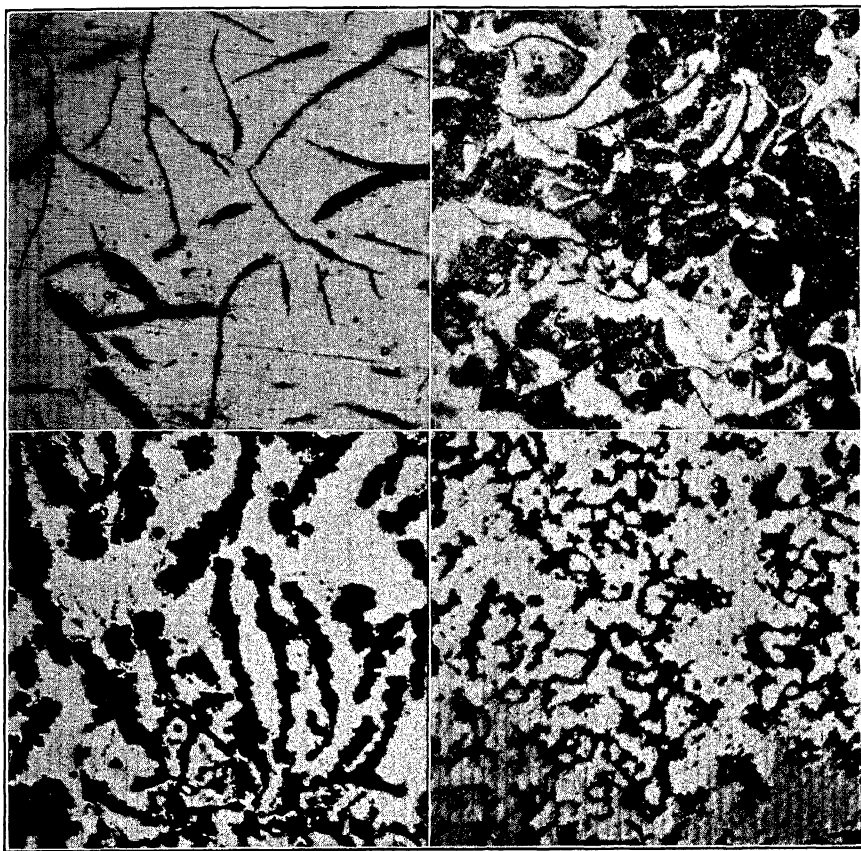
FIG. 4.—ORIGINAL SPECIMEN, UNETCHED. × 200.
FIG. 5.—ORIGINAL SPECIMEN, ETCHED IN NITRIC ACID AND ALCOHOL. × 200.
FIG. 6.—FURNACE-COOLED SPECIMEN, UNETCHED. × 200.
FIG. 7.—AIR-COOLED SPECIMEN, UNETCHED. × 200.

into larger graphite particles. A sufficiently long period of time at a high temperature had not elapsed to allow this coarse structure to be formed in the air-cooled and oil-quenched pieces. Fig. 9 illustrates a section of an ingot mold in the unetched condition. This sample was taken from the inside surface of the mold after the mold had been discarded from further service. The structure is approaching that of

the test pieces after repeated heatings. In the ingot mold the thermal treatment does not appear to be as severe as that shown in the specimens.

Some of the total growth is believed by the writer to take place in the following manner: Upon heating and holding the test bar at the elevated temperatures, some of the graphite is taken into solution through the general process of cementation, increasing in amount up to the eutectic temperature. Upon cooling this carbon which had been absorbed is again thrown out as graphite flakes, but since the graphite flakes cannot be formed in the void which remained as a result of the resolution, the new graphite flakes are born in a volume of previously solid metal. This graphitization would correspond to that of a cast iron in which the proeutectoid and eutectoid cementite breaks down into graphite and iron.
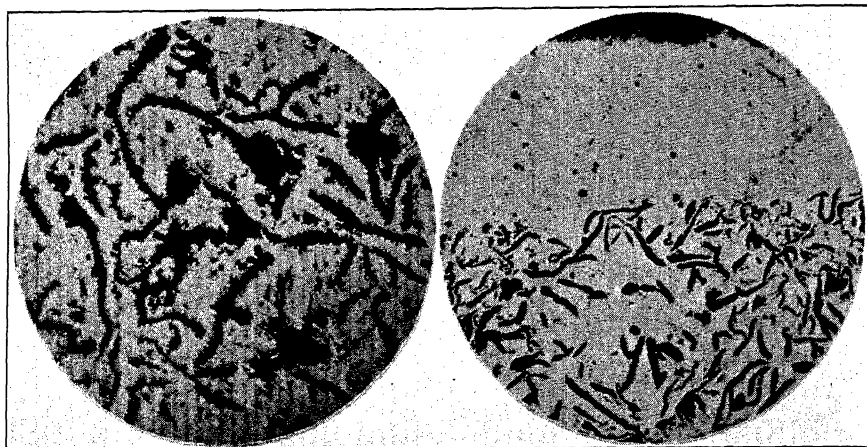
FIG. 8.—OIL-QUENCHED SPECIMEN,   FIG. 9.—INGOT MOLD SECTION ADJACENT TO
      UNETCHED.   × 200.   INSIDE SURFACE, UNETCHED.   × 75.

This cycle continues until a critical condition of sponginess is approached, after which any reprecipitation of graphite in virgin areas is taken care of by the internal distortion of the spongy skeleton work.

The increase in volume resulting from an increase in weight calculated in terms of cubic inches of FeO is very small. Considering the loss of carbon as being replaced by oxygen and making no allowance for the porosity of the cast iron—in other words, giving the benefits of all things which might be questioned to the oxygen—the increase in volume created by the added weight gives the following: furnace cool, 0.58 per cent. increase in volume; air cool, 3.2 per cent.; oil quench, 7.5 per cent. In view of the actually measured growth, these percentages are convincing that some explanation other than oxidation alone must be offered.

Since the previous work demonstrated that growth is not caused entirely by oxidation, further experiments were planned to test the other

theories of growth, particularly the ideas concerning occluded gases
Two experiments were originated   In the first the bar was heated and
cooled in a vacuum; in the second, the bar was heated and cooled in an
atmosphere of nitrogen   These experiments were conducted in a
standard type of laboratory tube furnace, using the same temperature
and holding period as before   A sufficient number of these runs was
made to establish the rate of growth

The results indicate that the rate of growth in the two cases men-
tioned is the same   Had the theory of entrapped gases been correct,
one would expect the bar heated in vacuum to grow more than the bar
heated in nitrogen   Since the bar heated in vacuum showed a decided
growth that could not be attributed to internal gas pressure because of
the corresponding determinations in nitrogen atmospheres, the theory of
entrapped gases seems in error   Two possibilities remain (1) repre-
cipitation of graphite, (2) mechanical enlargement caused by hair
cracks, resulting from stresses set up by nonuniformity of expansion
and contraction

One more experiment was made to determine whether one of the two
remaining phenomena was taking place, or possibly both   A bar was
heated and cooled in nitrogen as before but without holding at the
maximum temperature   The heating and cooling rates were identical
with those where holding time at the maximum was used   This bar
showed a rate of growth that was less than the rate for the bar that was
soaked at the maximum temperature for a definite length of time   Since
there was no holding time in the last experiment, it appears that the
time element necessary for cementation to a condition of equilibrium had
not been reached, and, therefore, the amount of reprecipitation was less
This indicates then that some of the growth can be attributed to the
reprecipitation of graphite, and since the oil-quenched bar grew at a
more rapid rate than the air-cooled bar, it appears that there exists this
condition of mechanical stressing, resulting in a minutely fractured
structure   It is needless to say that physical properties deteriorate
rapidly with growth.

Summary and Conclusion

The phenomenon of irreversible growth of gray cast iron can be
described as a result of.

1 Precipitation, solution and reprecipitation of graphite in the solid
matrix material.   Ordinarily this effect is predominant in the growth
obtained on the first heating after casting

2 Oxidation of the matrix material after the graphite flakes have
been burned out.   This reaction has a large accelerating effect on growth.

3 Mechanical swelling created by finely fracturing the slightly ductile
structure of gray cast iron   This fracturing is most effective on passing
through the A_1 transformation both on heating and cooling.

The effect of the various alloy elements can be summarized in a few statements   All alloying elements, such as silicon, aluminum and under certain conditions titanium and nickel, which favor the precipitation of carbon, tend to increase growth while elements such as chromium and manganese, which exert a stabilizing effect on the carbon, tend to decrease growth   Increase in total carbon also increases the growth   Vanadium, even though much less effective than the other precipitating elements, favors growth   Chromium, either alone or in the presence of vanadium or nickel, effects a retarded growth, particularly if the nickel is replacing some of the silicon in the cast iron

The foregoing summary indicates that in order to minimize growth the cast iron should be as near to a white iron condition as is practicable for the particular casting   Alloy cast irons, such as chrome nickel or chrome vanadium, produce a smaller amount of growth   With this as a preliminary step the castings should further be protected from excessive oxidation where possible and the temperature changes should be gradual

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      lurgy, 1927
35 See next page

DISCUSSION

(R F Harrington presiding)

J T MacKenzie, Birmingham, Ala —I agree with Mr Remmers in his summary stating the conditions that cause growth   However, I cannot reconcile causes 1, 2 and 3 with his statements in the last paragraph of the paper; for instance, that the effect of the alloys which cause the precipitation of carbon is to increase growth while elements such as chromium, either alone or in the presence of vanadium or nickel, effects a retarded growth, particularly if the nickel is replacing some of the silicon in the cast iron.   That is undoubtedly true after the metal is cast   However, if a large part of the growth depends in the first instance on the decomposition of pearlite, it would seem that the elements in the molten metal which favor the separation of graphite, or rather the diminution of combined carbon, would in the same manner tend to diminish the growth in the first stage of heating after the metal is cast

There has been some successful work with the Shutz iron, which is almost pure ferrite and graphite   This metal, of course, would only be subjected to growth from mechanical stress and from straight oxidation   The low-carbon metals which have been rendered pearlitic by silicon have been successful in growth, but silicon, by its oxidation, tends to disrupt the metal and to increase growth, so that the combination of low-silicon metal with comparatively low carbon cast in the hot mold has been successful

A word in regard to chromium If there is an excess of chromium, which gives the dendritic structure of cementite radiating in from the casting, it makes the metal very brittle and sensitive to mechanical stresses, the metal cracks rapidly, especially when there is heating on one side   In cooling, the metal tends to crack the hot side; also, if the metal is hard, it will not yield on the cold side when it is being heated up, so cracks develop on both sides

C O. Burgess, Long Island City, N Y —In using chromium in cast iron to retard growth, we find that with a small percentage of chromium, just sufficient to produce a completely pearlitic iron and not an excessive amount of cementite, the growth is practically eliminated   We have not come across the effect that Mr Mac-Kenzie speaks of

H A Schwartz, Cleveland, Ohio (written discussion) —If Remmers' view on this point is justified, it should be possible to see, in the microstructure of irons which have grown, considerable amounts of nodular carbon   In the special case where the original combined carbon is absent, a condition approached somewhat in Remmers' metal, any nodular free carbon would prove the author's contention   It would be interesting to know whether such nodular carbon was in fact definitely known to exist and to increase during the experimental procedure

It is not my intention either to support or attack this particular portion of Remmers' theory, but it may be well to point out that it has been experimentally shown that malleable cast iron, when completely decarburized after graphitization by heat treatment in moist hydrogen, decreases in volume, because the places previously occupied by graphite do not remain as holes but actually close up   If this observation is general, Remmers' theory would fail, because recombination of carbon would produce exactly the decrease of volume that would exactly balance the increase due to the subsequent reprecipitation of the corresponding carbon content

R F Harrington, Boston, Mass —An interesting direction of effort would be to study two irons of exactly the same composition, but cast in test bars of different dimensions   If you take a 4-in test bar, for instance, and compare the growth of that bar with the growth of a bar of 1 in dia , cast from the same iron, I believe that the growth of the bar of larger diameter will be less than the growth of the bar of smaller diameter.   Have you tried any work in this connection?

W E Remmers —No attempt has been made in this investigation to study the effect of test-bar dimension upon growth

Mr MacKenzie undoubtedly is correct in his discussion of the effect of various elements on volume changes   This paper deals with a study of growth as found in previously cast gray iron and does not consider volume changes at solidification and initial cooling from the casting temperature   In this work upon gray iron, nothing was done with the high-chromium white iron mentioned by Mr MacKenzie   The growth of low-chrome, gray cast iron has already been described by Mr Burgess

No work has been done on malleable iron as described by Dr Schwartz   The closest approach to his work was the heating of gray iron in an atmosphere of commercial hydrogen without adding any moisture   A decided growth rather than shrinkage was noted.

Since the writing of this paper in December, 1929, some very noteworthy literature upon the subject of growth has been published [35]

J T MacKenzie —The amount of the graphite is not so important in the heat-resisting iron as the distribution, and I am afraid that on your large bar, for instance, you would find that the graphite would be present in larger flakes and thus oxidize more readily   Where the graphite is in finely divided form, there are more or less disconnected shapes and the oxidation has to plow its way through the matrix before it can get to a new flake

Also, these tests are all made without any stress on them   It has been found, for instance, that whereas an unstressed cast iron did not grow on a 200° rate in steam, if stressed to a point of approximately 35 or 40 per cent of its strength it did show pronounced growth in live steam at 200° C , so that effect could not certainly be overlooked

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[35] J S Vanick and P D Merica Corrosion and Heat-resistant Nickel-Copper-Chromium Cast Iron   *Trans* Amer Soc. Steel Treat (1930) **18**, 923

R S MacPherran and H. Krueger Long Heating Periods at High Temperatures Affect Gray Cast Iron   *Foundry* (1930) **58**, 103

W E Remmers ---In line with the discussion on the size of test bar, I may add a point that probably has a very direct bearing on the subject   The high-silicon test bars that were used, contained at the beginning of the work, as I recall, 3 32 per cent total carbon   At the end of the series of 25 repeated heatings in an atmosphere of combustion gases, resulting from the burning of water gas, the total carbon of the material upon several analyses varied from 0 04 to 0 09 per cent, which indicated clearly that the graphite had practically all disappeared in the dark areas that were noted on the last photomicrograph   These dark areas do not represent graphite, of course, but principally voids and oxides   If oxides were there originally, in the polishing much had dropped out, and the areas as we saw them on the slides consisted principally of voids

Some Notes on Blue Brittleness

By Leland Russell van Wert,[*] Cambridge, Mass

In 1888, Howard,[1] working at the Watertown Arsenal on the tensile properties of ferrous materials at various temperatures, noted the curious fact that the stress-strain diagrams of low-carbon steels tested within a certain temperature range (200° to 350° C) departed more or less from the normal regularity of such diagrams as secured by testing at either above or below these temperatures   This same jagged appearance of similar diagrams for steels has been observed by at least one other investigator, and de Forest[2] has reported similar irregularities in the tensile testing of some nonferrous alloys   Recently again, this anomaly in diagram contour has been shown in a most striking fashion, apparently because of its accentuation by the method of testing employed, by Dr Albert Sauveur [3] He described (for nonaustenitic steels) two quite distinct types of torsional stress-time diagrams   (1) those with a regular and smooth outline, derived normally by testing at temperatures above 300° C , or below 200° C (as, for example, Figs 4a or e), and (2) those presenting a decided "stepped" appearance, which are invariably produced when twisting is done within the 200° to 300° C range (examples, Figs 5a and b)   The torsion test brings out so much more sharply (and convincingly) the irregularities occurring at 200° and 300° C than does the tensile test that they can no longer be considered as resulting from simply idiosyncratic or accidental and inconsequential causes

Clearly, from the temperatures involved, the "stepped" type of diagram, or more accurately, the peculiar manner of response to torsional stress which manifests itself in the diagram, is an aspect of the "blue-heat" phenomenon   One's curiosity, if nothing else, prompts an inquiry as to the nature and significance of these "steps "   What do they mean? What causes them?   To these questions there are no completely satisfactory answers.   The following experimental observations are offered as suggestions towards the solution of the problem.

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[*] Assistant Professor of Metallurgy, Carnegie Institute of Technology   Lecturer in Metallurgy (1930–31), Harvard University
[1] Howard· Report on Tests of Metals, 243   Watertown Arsenal, 1888
[2] A V de Forest Some Experiments on the Plastic Elongation of Wire   *Proc A S T. M* (1916), 16[2], 455
[3] A. Sauveur Steel at Elevated Temperatures   *Trans* Amer Soc Test Mat (1929) **17**, 410

SIGNIFICANCE OF STEPS IN TERMS OF TORSIONAL STRAIN

The stepped stress-time diagram clearly indicates that under a uniformly increasing load deformation does not proceed regularly, but rather that there are periods of deformation alternating with periods of little or no (inelastic) yielding   In other words, progress toward fracture of the specimen occurs in this wise. as soon as the true elastic limit or yield point is exceeded, the bar deforms a certain amount, then—to all appearances and in view of its subsequent behavior—apparently recovers its elasticity [and yield point (?)]   This is followed by a probable though small elastic deformation,[4] again a sudden yielding as loading exceeds the new "elastic limit," and finally this is again brought to a full stop through
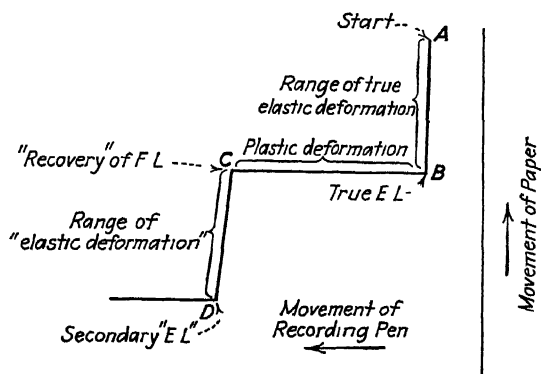
FIG 1 —IDEAL "STEP" IN STRESS-TIME DIAGRAM.

a second "recovery" of the elasticity   This three-stage cycle continues until fracture ensues   A diagram of an ideal three-stage cycle is shown in Fig 1.

The relative "lengths" of the periods when the bar is undergoing the small amount of elastic deformation (*AB* in Fig 1), and those of the yielding periods (*BC* of Fig. 1), increase as loading proceeds.

It is now generally believed that aging after overstrain and blue brittleness are but different manifestations of one and the same phenomenon.   One of the best known effects of aging following overstrain is the recovery of the elastic limit[5] which is made to approach an extremely low value by the working operation [6,7]   As a matter of accuracy, as van den Broek has shown, the recovery may be considerably over 100 per

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[4] Some of this elastic yielding is, no doubt, due to a certain amount of give in the torsion machine

[5] J A van den Broek: The Effects of Cold-working on the Elastic Properties of Steel   Iron and Steel Inst. *Carnegie Schol. Mem* (1918) **9**, 125–168

[6] J A van den Brook *Loc cit*

[7] L Aitchison· The Low Apparent Elastic Limit of Quenched and Work-hardened Steels   Iron and Steel Inst *Carnegie Schol Mem* (1923) **12**, 113–217

cent., that is, the strained and aged steel may have a much higher "elastic limit" than it possessed originally.

The recovery of, and the augmentation to the original elastic properties on aging after overstrain requires a considerable period of time— a question of days—if aging is permitted to take place at ordinary temperatures   The time necessary, however, becomes much shortened with somewhat higher aging temperatures   Van den Broek's and, in particular, Muir's[3] work have shown that the elastic recovery at 100° C is as complete after a few minutes as in two weeks at ordinary temperatures, and at 250° C it becomes a question of seconds or even fractions thereof

With these experimental facts as a background, it requires no unusually active imagination to picture the so-called blue-brittle phenomenon as merely a specific and particular case of aging, where at the temperatures used, aging follows straining so closely that its effects, normally requiring days to attain to a maximum, do so instantly   The fact that the deformation takes place not at room temperatures but at the higher blue-heat temperatures is of no consequence as far as actual aging rate is concerned, the temperature of deformation becomes important, as it does at temperatures above blue heat, only when, through softening of the steel (ferrite), the strain induced is insufficient to initiate what the author believes is the *modus operandi* of the blue-brittle phenomenon; namely, the precipitation of discrete "keying" particles

If this is the true picture of the essential oneness of aging and blue brittleness, is it not logical to conceive of the sudden arrests in twisting, as recorded in the steps, as due to an apparent *recovery* of the elastic properties, of the same manner of recovery as that found by van den Broek on aging following overstrain?   In this instance, of course, the recovery of elasticity is instantaneous, or practically so, whereas van den Broek, working at lower temperatures (room temperatures and 100° C) found that some appreciable time was necessary   But it is a question of temperature, and in view of Muir's results, showing a practically instantaneous rate of aging at blue-heat temperatures, the assumption is warranted here

That it is an apparent and not a true recovery of the elastic limit— and this reservation applies likewise to van den Broek's results—will be seen from the answer to the question as to the probable cause of the steps, or rather the irregular yielding recorded in the steps.

The idea that the recovery of a pseudoelastic limit may explain the stepped character of the stress-time diagrams of bars twisted in the temperature range where aging is reputedly exceedingly rapid (200° to 300° C) may seem more reasonable and convincing after the answer

[3] J. Muir. On the Recovery of Iron from Overstrain   *Phil Trans Royal Soc.* (1900) **193A,** 1–46.

to the second question is given   Fortunately, this answer rests on the more secure foundation of experiment

CAUSE OF STEPS

Aging after overstrain, and blue brittleness, are undoubtedly the result of dispersion hardening [9-12]   There is too much evidence to lead one to believe otherwise   The disperse phase, precipitated from its solid solution in ferrite by straining,[13] and acting as keys (Jeffries), or as a distorter of the ferrite space lattice (Rosenhain et al), is probably ferrous oxide (FeO),[14] iron carbide (Fe_3C),[15] or an iron nitride [16,17]   The Fe-O, Fe-C and Fe-N systems all show the necessary condition demanded of age-hardenability in a system, viz , a marked decrease in solid solubility with decrease in temperature, and it is most likely that aging and blue-brittle effects result from the dispersion of one or all of these elements in combination as given   Since the stepped character of torsional diagrams results from a response to stress which is apparently peculiar to ferrite (proeutectoid and eutectoid) within the blue-heat range of temperatures, iron completely free from these suspected impurities should show no stepping when twisted at 200° to 300° C   On the other hand, it would seem a reasonable possibility to find circumstances involving solid solution relations of the above mentioned oxygen, carbon or nitrogen, that would yield blue-brittle effects (stepping) at temperatures distinctly outside the usual blue-heat range

Unfortunately, no way is known of making an iron that will be absolutely free from one or all of the elements in question, and equally disturbing is the fact that the small amounts that inevitably remain after the most careful processing can exert relative disproportionate effects   An iron unquestionably most free from carbon, oxygen and nitrogen (and other contaminating elements as well) is that made by Dr T. D Yensen of the Research Laboratory of the Westinghouse Electric and Manu-

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[9] L B Pfeil The Change in Tensile Strength Due to Ageing of Cold-drawn Iron and Steel   Jnl Iron and Steel Inst (1928) 118, 167

[10] R S Dean, R O⁻ Day and J L. Gregg Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-nitrogen   Trans A I M E , Iron and Steel Div (1929) 446

[11] W Koster Effect of Quenching and Drawing below the A_1 Point upon the Physical Properties of Fe-N Alloys   Metals & Alloys (1930) 1, 571-5

[12] G Masing Vergutbarkeit von Legierungen und neuartige Alterungserscheinungen beim Eisen   Archiv f d. Eisenhuttenwesen (1928–29) 2, 185

[13] W Koster· Zur Frage des Stickstoffs im technischen Eisen   Stahl und Eisen, (1930) 50, 629

[14] L B Pfeil Loc cit

[15] L B Pfeil Loc cit

[16] R S Dean, R O Day and J L Gregg Loc cit

[17] W Koster· Reference of footnote 13

facturing Co for use in his well-known magnetic work   A small piece of this high-purity iron, which contained carbon below 0 005 per cent , oxygen about 0 01 per cent and nitrogen about 0 005 per cent , was secured from Dr. Yensen   Torsion bars made therefrom were tested at room and higher temperatures   The stress-time diagrams of the bars tested at room temperatures were of the normal smooth and regular contour type similar to those shown in Figs 4a or e   The diagram of the 300° C test is that given in Fig 2   It is a decidedly irregular curve but not of the sharp steplike characteristics of the usual diagram of the 300° C test   For example, the juxtaposition of contiguous steps is not at right angles   There is less evidence of a definite elastic deformation between the successive periods where major inelastic (plastic) deforma-tion occurred   There is actual creep between the periods of major movement and not the almost imperceptible elastic yielding usual at 300° C   Why these differences from the usual diagram made at 300° C ?
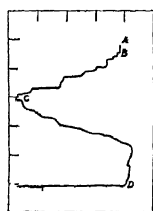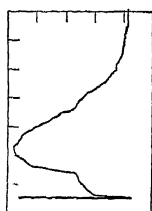
Obviously, the impurities (in this case, oxygen principally, because it is the major impurity) supposedly responsible were in-sufficient in amount to accomplish the full effect of a pseudoelastic recovery; namely, (1) bringing the plastic deformation to a full stop, and (2) retaining the "elasticity" re-covered over a reasonable period of time under a uniformly increasing load. In this case of "pure" iron the first has been done but not the second. That this is the correct explanation becomes evident on close examination of the diagram   This diagram may be divided into three portions AB represents true elastic deformation, the elastic limit (or yield point, since it is impossible or impractical to distinguish between the two in the test) is exceeded at B, BC represents the early stages in the inelastic (plastic) deformation of the bar   In the first two or three steps of this portion of the diagram, there is a more complete "recovery" of elastic properties than later, that is, in this early part of the diagram the part of the steps which roughly parallel the direction of movement of the recording paper are, in fact, parallel   This indicates little, if any, but an elastic yielding   After the first two or three steps, the close parallelism no longer is in evidence, and in the final portion of the diagram (CD) even definite steps are missing.

Does not this ready divergence from the usual 90° angular placement of the steps indicate how soon in the twisting operation the extremely small amounts of impurities of this iron are exhausted as age-hardeners? As restorers of a pseudoelastic limit, are they not, because of their small amounts, effective only in the early stages of deformation, after which,

FIG 2   FIG 3.

FIG 2 —PURE (YENSEN) IRON TWISTED AT 300° C
FIG 3 —IZETT STEEL TWISTED AT 300° C

in then "effective" absence, deformation proceeds in a smooth, regular and truly inelastic manner?

An interesting steel, in this connection, is Izett, a nonaging steel originated by Krupp's Its extremely low susceptibility to aging (and to blue brittleness) is said to be due to its low *dissolved* oxygen content, a circumstance resulting from its method of manufacture This steel when twisted at 300° C gave a stress-time diagram as shown in Fig 3 Scarcely perceptible steps, but with true 90° angles, occur early during deformation, an irregular creeping thereafter. The whole curve is much smoother than the one found for Yensen iron If the explanation given of causes is correct, this diagram shows how remarkably free Izett steel is from dissolved impurities (reputedly oxygen)

Incidentally, the presence of carbon in Izett (this one carried 0 13 per cent) apparently removes this element from among those that have usually been thought as probable causes of aging and blue brittleness It is difficult to see how the equilibrium solubility of carbon in ferrite in Izett should be different from that in similar commercial mild steels, since the occurrence of the precipitated carbon, the Fe_3C of the pearlite, with which the dissolved carbon is in equilibrium, is identical in the two steels, whereas this condition need not necessarily apply to the oxygen because the nature of the precipitated oxide (and its solid solubility in ferrite) in the two steels obviously will differ with the oxidizer used in the manufacture of each

The maximum solid solubility of oxygen or carbon in ferrite is ridiculously small, of the magnitude of 0 04 to 0 05 per cent This high value obtains at the temperature of the respective eutectoids, at lower temperatures the solubility becomes progressively lower, down to an almost vanishing figure at room temperatures Because of the low maximum values of solid solubility, the amounts of precipitated oxide or carbide involved in age-hardening are extremely small, and thus require the most favorable conditions (i e , a temperature of 200° to 300° C) to develop effectively their ability to restore what we have assumed is a pseudo-elastic limit It seemed reasonable to believe that in an age-hardenable iron alloy with a relatively large maximum solid solubility (a question of tenths rather than of hundredths of one per cent.), one should obtain, simply because of greater quantities of hardener involved, an apparent elastic recovery (and other aging effects, such as a lowered ductility) at temperatures outside (below) the unusually and uniquely propitious 200° to 300° C range Nitrogen-iron alloys fulfill these conditions, since the alloys are age-hardenable and the maximum solid solubility of nitrogen in ferrite is comparatively high (about 0 5 per cent.) at the eutectoid temperature (580° C.). The solubility also is low at room temperatures, in the neighborhood of 0.015 per cent., thus giving a wide range in solid solubility.

Standard torsional test specimens of Armco iron were nitrided in the usual way (in ammonia, at 975° F. for 48 hr) and slowly cooled in the nitriding furnace   Microscopic examination of the reduced cross-section of the bar (¼ in dia) revealed many iron nitride needles, distributed from outside to nearly the center   One set of bars was twisted as nitrided, that is, after slow cooling   These bars, of course, had but a small amount of nitrogen in solution, probably not far above the equilibrium amount at room temperature).   The stress-time diagrams of the series twisted at room temperature, at 100°, 200°, 300° and 400° C are shown in Fig. 4 In general, the results are in accordance with expectations in view of the small amount of dissolved nitrogen.   The bars required the favorable
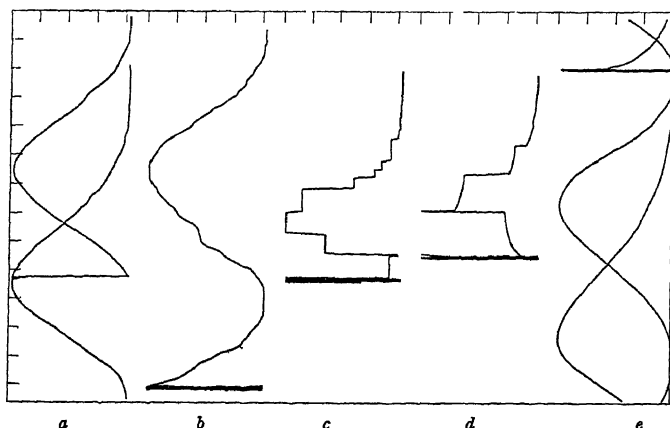
FIG 4 —ARMCO IRON, NITRIDED AND SLOWLY COOLED
a Twisted at room temperature   d Twisted at 300° C
b Twisted at 100° C   e. Twisted at 400° C
c Twisted at 200° C

200° and 300° C temperatures to develop blue brittleness (as would be indicated in the torsional properties), and to reveal the stepped character of the stress-time curves

The diagram of the test at room temperature (Fig 4a) is a normal smooth curve; that of the 100° C test (Fig 4b) reveals some departure from the smoothness of the preceding, and also from the smoothness of the usual diagram obtained by twisting plain Armco iron at 100° C. Doubtless the larger than normal amounts of nitrogen in solution made possible through the nonattainment of complete equilibrium on cooling account for the premature development of abnormality in diagram contour.   The tests conducted at 200° and 300° C. (Figs. 4c and d) show characteristic stepped curves   Twisting at 400° C gave the smooth and regular curves usual for that temperature and for those immediately above.

The second set of the nitrided bars were water-quenched from 575° C., that is, from near the temperature where solid solubility of nitrogen in

ferrite is at the maximum   Microscopic examination did not reveal a single needle   These bars were twisted at room temperature and at 100°, 200°, 300° and 400° C   Twisting at room temperatures gave a decidedly stepped diagram (Fig 5a)   There was the same result from twisting at 100° and 200° C (Figs 5b and c)   Twisting at 300° and 400° C gave smooth curves (Figs 5d and e), the latter in accordance with

a   b   c   d   e
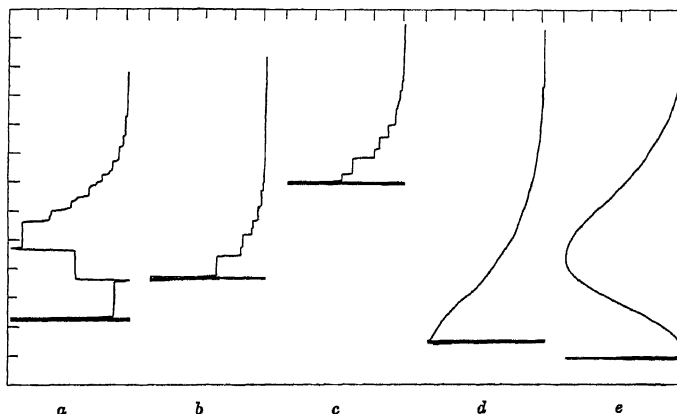
Fig 5 —Armco iron, nitrided and quenched in water at 575° C
a Twisted at room temperature   d Twisted at 300° C
b Twisted at 100° C   e Twisted at 400° C
c Twisted at 200° C.

expectations, the former quite the contrary   What has happened in this nitrided and quenched series is that stepping and its obvious cause—alternate yielding and apparent elastic recovery—take place at temperatures (room and 100° C) below the point at which they ordinarily occur The displacement of the blue-heat range to lower temperatures is again shown in the physical (torsional) properties of the two series (Table 1)

TABLE 1 —*Torsional Properties*

Twisted at, Deg C	Not Quenched		Quenched	
	Angle	Load	Angle	Load
20	2 00	31 8	1 17	48 4
100	1 42	30 2	0 29	54 2
200	1 24	35 0	0 33	47 4
300	0 83	35 4	0 46	54 6
400	2 31	21 7	1 03	29 4

In the not-quenched nitrided series the minimum ductility occurs at 300° C with an angle of 0 83   The maximum torsional load also occurs here.   One has then a normal case of blue brittleness   In the quenched series, the minimum angle occurs at 100° C   The load at 100° C. is also

high but practically equals that (the maximum) at 300° C. There is no doubt that maximum brittleness, taking both angle and load into consideration, occurs in this series at 100° C. (or in that neighborhood), an occurrence that is most easily explained by the unusually large amount of the hardener in solid solution, and in the greater metastability of that solution with its consequent greater tendency to break down at lower temperatures. "Blue brittleness" as a generic name for the phenomenon may, after all, be a misnomer, and applicable, in a strict sense, only when small (usual) amounts of hardener are present

The reasons for specifically designating the probable cause of the steps as an apparent elastic recovery are now clear   The elastic limit is an inherent property of pure metals   It is difficult to see how cold working, which at first greatly lowers the elastic limit, could, in effect at least, eventually restore it and actually increase it beyond the original value   The recovery of elasticity on aging at room temperatures, or the relatively faster recovery at somewhat higher temperatures, as van den Broek found, is, in the author's opinion, more apparent than real   To him, aging after overstrain affects the elastic properties of ferrite not by the actual restoration of the true elastic limit, which is largely lost on deformation, but by producing through the peculiar mechanism of dispersion hardening, as described, an effect that simulates that recovery And when that apparent recovery becomes practically instantaneous at blue-heat temperatures, as it does with ferrite solutions with usual concentrations of dissolved hardener, or at lower temperatures where high concentrations result in a greater metastability, the stress-time diagrams take on the steplike character noted

DISCUSSION

(R. F Harrington presiding)

R. F MEHL AND C W. BRIGGS, Washington, D C (written discussion) —Dr van Wert follows tradition in identifying aging with blue brittleness, and presents some new and interesting facts on the relation of stepped yielding to the aging process in iron and steel

The identification of aging with blue brittleness goes back many years   Fettweis[18] ascribes the original idea to A Le Chatelier, first conceived before the turn of the century.   Fettweis extended and amplified Le Chatelier's idea so capably that his paper is now recognized as the classic in the field

The conception that aging and blue brittleness are different manifestations of the same process, differing only in the speed at which the strengthening and embrittling process proceeds—a speed which is very great at the bluing temperatures, 200° to 300°, but low at room temperature—has only once been brought seriously into question.   Korber and Dreyer pointed out[19] that the brittleness developed on aging at room temperature and that developed in the blue-brittle range are quantitatively

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[18] Fettweis Stahl und Eisen (1919) **39**, 1, 34
[19] Korber und Dreyer: Mitt Eisenforsch (1921) **2**, 59

greatly different and suggested that for this reason the two processes should not be considered as identical

This objection has not been accepted generally, for it may be easily conceived that the same process operating at different temperatures should lead to different degrees of brittleness, much as aging at different temperatures in alloys of the duralumin type lead to different strength and ductility values

The conception that aging and blue brittleness are both caused by a precipitation from a solid solution seems to be upon much less certain ground than might be suspected from Dr van Wert's account   The idea seems first to have been presented by Ludwik[20] and later amplified by the workers listed by Dr van Wert on page 233

The evidence now available in support of this conclusion is as follows·

1 The action of Fry's etching agent on low-carbon steels which have been given the duralumin type of heat treatment and subsequently aged, inducing a process which is almost certainly identical in type with that occurring in duralumin, is such that the alloy is progressively more strongly blackened as its strength and ductility values indicate the progression of the aging process   A similar blackening by Fry's etching agent occurs when an overstrained steel heated in the blue-brittle range is treated   The darkening obtained on the steel given the duralumin treatment is assumed to be indicative of a precipitation process, and by analogy that on the steel given the blue-brittleness treatment is also assumed to be indicative of a precipitation process

2 The rapid decrease in the notch-impact value in the neighborhood of 0° C characteristic of iron and steel is displaced towards higher temperatures when iron-copper alloys, which are alloys capable of duralumin hardening, are caused to age   The effect of the blue-brittleness type of treatment is to produce a qualitatively similar displacement towards higher temperatures, and by analogy this displacement also indicates the operation of a precipitation process

3 It seems likely that blue brittleness is related to the presence of one or more of the elements C, O, and N present in steels   Each of these elements is known to show an increasing solubility in ferrite with increasing temperature, the condition necessary for age-hardening of the duralumin type   It is concluded, therefore, that the *modus operandi* of these elements in the embrittlement of steel is one of precipitation

This is one side of the picture   Before criticizing it, let us state immediately that it is the best explanation now available

It is soon apparent that the evidence cited above is all indirect   Evidence has not yet been presented that during the process of aging or blue-embrittling a solid solution decomposes and precipitates a new phase   Furthermore, there is one characteristic of the aging and blue-brittleness process that is unusual and very striking, a characteristic peculiar to it alone and not to alloys of the duralumin type, namely, it requires plastic deformation for its initiation

It is not an easy matter to construct experimentation to prove that a solid solution decomposes during aging or blue-embrittling   Such tests as might be set up are inevitably confused by the necessary plastic deformation   If the classic criteria of density, lattice parameter and electrical conductivity are set up, the effect of the deformation is to obscure the meaning of any data obtained

But the requirement of initial plastic deformation is perhaps the most puzzling. If purely a precipitation process, it would be expected that extremely slow cooling would diminish if not entirely remove the aging potentiality, yet H. M Kaiser, at our laboratory, has shown that a piece of low-carbon steel cooled from A_1 in the furnace and another cooled from A_1 to room temperature over a period of 111 hr. both

[20] P Ludwik· Streckgrenze, Kalt-und Warmsprodigkeit   *Ztsch*. ver deut Ing (1926) **70**, 379

aged after cold work to identical degrees   It would seem an unavoidable conclusion that the state of equilibrium of the alloy with respect to possibly potential precipitating constituents is relatively unimportant

This point of view might be extended, as several workers have shown, with the assumption that (1) the rate of precipitation of the aging constituents is extremely slow, requiring deformation to accelerate it to appreciable rates, or (2) the effect of deformation is to render the aging constituents less soluble than in an unstrained alloy and thus to engender precipitation

This, we believe, represents fairly all that can be said with certainty concerning the mechanism of aging and blue-embrittling   It is obvious that it contains but little real knowledge.

Whatever the mechanism of aging and blue-embrittling may be, the question of the agents responsible for it is industrially of the greatest importance   Here again, there is great uncertainty

It has always been assumed that aging and blue brittleness are *not* a property of pure iron   It might be well always to keep this assumption clearly in the foreground until its proof is furnished   The ground for this assumption is simply that the sensitivity to aging decreases as the purity of the steel increases   No sample of iron has yet been prepared entirely free from aging and blue brittleness

One method of studying the effects of the various constituents in steel immediately suggests itself, namely, to prepare *pure* binary alloys of iron with the elements usually present in commercial steel and to test these for aging sensitivity   It is a fair statement that though such studies have been attempted not one of them is free from serious objection   The difficulty, of course, is very familiar   it is nearly impossible to prepare iron alloys free from small quantities of oxygen, nitrogen, carbon, etc

In fact, the results from an investigation of the aging of pure binary alloys of iron, though valuable and from a scientific standpoint necessary, could be applied to commercial alloys only in a limited fashion   Thus, if it were shown that C, Si, P, Mn and Cu are not effective in binary alloys, but that N and O are, it could not be concluded that this also should hold for ordinary steels where all these elements are present at one time, for the mere presence of another element might well render the first effective through, let us, say, an alteration in the first element's solubility in ferrite   The effect of additional elements upon the solid solubility of two metals is well known and need not be stressed—the presence of Si, for instance, profoundly alters the solubility of Mg in Al [21]

Such a circumstance would answer Professor Sauveur's question on the effect of N upon the aging of Izett, to which he referred a few years ago in his Campbell lecture.   It is possible that the appreciable quantities of N found in Izett are rendered less effective by the presence or absence of other elements

Little attention ordinarily is given to the effects of inclusions on aging sensitivity, though several years ago Fry[22] classified the various inclusions in this respect   Fry concluded that Al_2O_3 induced no aging sensitivity—because, he believed, it did not dissolve in ferrite and on aging reprecipitate but that MnO, FeO, the oxides of vanadium and the various silicates did induce such a sensitivity

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[21] A notable example of this type of interaction which has recently been pointed out by Fell (Untersuchungen uber den Einflusz von Sauerstoff und Schwefel auf die Schmiedbarkeit, Rotbruchigkeit und andere Eigenschaften des reinen Eisen   Dissertation, Dusseldorf, 1931) is a somewhat similar problem   Fell demonstrates experimentally that sulfur and not oxygen is responsible for red shortness, but that the amount of sulfur necessary for red shortness is dependent upon the amount of oxygen present, decreasing as the amount of oxygen increases

[22] A. Fry. Discussion, *Archiv f d Eisenhuttenwesen* (1929) **2**, 735

Izett—the alloy produced in Germany reputedly free from aging—is in fact not free from aging or blue brittleness, it is merely less sensitive, it shows both aging and blue brittleness to a diminished degree   This has already been shown by Bauer,[23] using the notch-impact test   There are no other studies on the aging and blue-embrittlement sensitivity of Izett, so far as we are aware, though these would be extremely interesting

Blue brittleness is usually thought of in terms of the tensile test   In order to fit Izett into this familiar mental picture we (with the help of Mr Gezelius of our laboratory) have made measurements of tensile strength, elongation, and reduction of area at a series of temperatures   The results of these measurements are shown in Fig 6
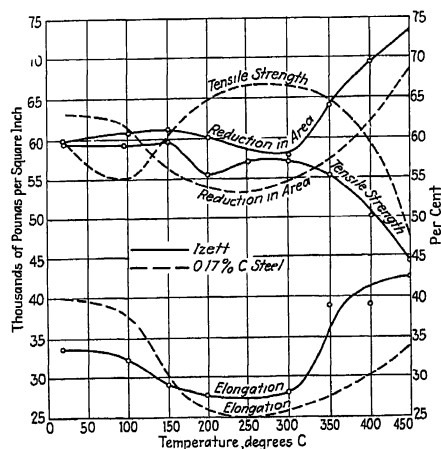
FIG 6   FIG 7

FIG 6 —RESULTS OF MEASUREMENTS OF TENTILE STRENGTH, ELONGATION AND REDUCTION OF AREA AT A SERIES OF TEMPERATURES
FIG 7 —VARIATION OF TRUE BREAKING LOAD
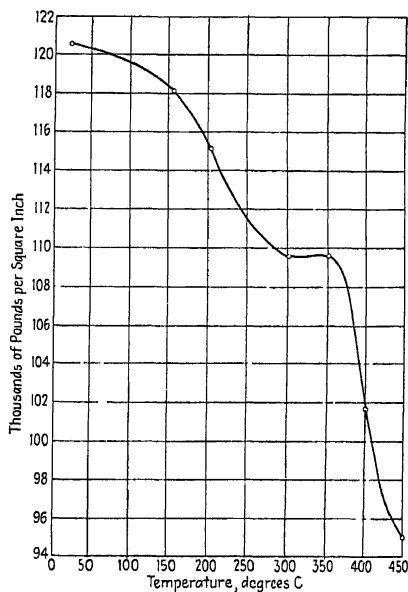
For purposes of comparison similar curves are introduced for a steel of approximately the same chemical composition and condition   It may be seen that the tensile strength of Izett shows little if any effect from blue brittleness   The elongation and reduction of area, however, show the effect pronouncedly, though not so markedly as do the similar values for the ordinary boiler steel [24]

The curve showing the variation of true breaking load—the ordinary breaking load corrected for reduction in area—is somewhat interesting (Fig 7)   In this case a pronounced maximum may be detected but at a temperature (350°) somewhat higher than the usual temperatures of blue brittleness

[23] Bauer *Mitt d Vereinigung der Grosskesselbesitzer* E V No 15 (Nov 20, 1927)

[24] It is interesting that similar curves given by McPherrhan [*Chem & Met Eng* (1921) 24, 1153] for Ni-Cr steels (2 4 per cent Ni, 0 38 per cent Cr, 0 34 per cent C) and high-nickel steel (33 per cent Ni) are much like the curves obtained here for Izett From this analogous behavior it might be expected that these alloy steels would show low aging sensitivity (as indeed the 3 or 5 per cent nickel boiler steel does).

It may be said, therefore, that so far as the properties determined in the tensile test are concerned, Izett is blue brittle, but not so blue brittle as ordinary steel of similar composition

It seems clear that the other type of aging in steel, the duralumin type, produced by the duralumin type of heat treatment discovered a few years ago in iron and steel by Masing and Koch,[25] and by Koster,[26] is produced by carbon for the effect is profoundly affected by variations in carbon content, the solubility of carbon in ferrite decreases with decreasing temperature, and electrolytic iron (nearly free from carbon but containing considerable oxygen) does not show the effect   Dean, Day and Gregg in this country had previously shown that nitrogen behaves in a similar way

If carbon or carbon plus nitrogen causes this type of aging, it becomes a question as to whether these elements are effective both in this type of aging and in the usual type of aging associated with blue brittleness, or whether the two types are distinctly separate and probably caused by distinctly different agents

In order to study this question, steel of the S A E 1010 composition was given a standard treatment for the production of aging—deformed 5 per cent and heated to 150° for various lengths of time, and the hardness measured as a function of the time This gave a curve representing the aging sensitivity of the material   Similar tests were run on the same steel when the treatment was such as to produce the duralumin type of treatment, i e , a quench from just below A₁ (668°) followed by aging at a moderate temperature, again establishing a standard curve of aging sensitivity, this time for the duralumin type of aging   Then a piece was given the duralumin type of treatment but far overaged, so that all the duralumin aging potentiality had been lost and the original hardness regained   This last specimen when given the standard aging or blue-brittleness treatment gave a curve closely similar to the first curve obtained   In other words, the steel behaved as though the exhaustion of the duralumin aging sensitivity had no effect upon the aging or blue-embrittling sensitivity, as though the two processes were in no wise related   Our results on this are still only preliminary, but should appear in print later

But to return to Dr van Wert's paper, especially for a consideration of stepped yielding   We are inclined to agree with Dr van Wert's explanation of this phenomenon   The torsional method of testing in the hands of Professor Sauveur and his students has yielded a great deal of information concerning the properties of steel at high temperatures   It has some inherent disadvantages, however, which should be pointed out   The chief disadvantage lies in the fact that the shearing stress is not uniform over the cross-section of the test pieces, it varies from a maximum at the surface to zero at the center   Stepped yielding is doubtless caused by a sudden yielding when the shearing stress reaches some threshold value at a particular spot in the piece, i e , at some definite distance from the center   From the fact that there is a radial stress gradient, however, it is impossible to decide the magnitude of this threshold shearing stress, therefore, for an analysis of stresses the torsional method is inherently disadvantageous   A simple tension method would appear preferable, if the apparatus for measuring elongation could be made sufficiently sensitive   Nevertheless, the torsional curves show stepped yielding more pronouncedly than any others we have seen, and if stepped yielding should prove to be unquestionably intimately connected with aging and blue brittleness the method will be of real value as a qualitative test for the susceptibility of steel to these types of behavior

Stepped slip is not new, as Dr van Wert states   It is an interesting fact that crystals of NaCl under tension show a remarkable stepped yielding [27]   Several years

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[25] Masing and Koch The Aging of Quenched Steel   *Wiss Veroffent a d Siemenz-Konzern* (1927) **1**, 202

[26] W Koster *Archiv f d Eisenhuttenwesen* (1928–29) **2**, 505

[27] A Joffe The Physics of Crystals. New York, 1928   McGraw-Hill Book Co

ago Lester and Aborn published a valuable paper, too little known, entitled "The Behavior under Stress of Iron Crystals in Steel," and demonstrated a striking stepped yielding between proportional limit and the yield point In fact it seems highly likely that the formation of Luder lines is simultaneous with stepped yielding Some attempt, then, should be made to correlate all these phenomena aging, stepped yielding, the drop of the beam at the yield point, stretcher-straining, Luder lines, and the stress figures brought out by Fry's etching agent Dr van Wert's demonstration of the stepped yielding effect, especially as embodied in Figs 4 and 5, is a real contribution, and it is to be hoped that he will continue and at a later time show some additional facts

T D YENSEN, East Pittsburgh, Pa (written discussion) —It seems logical to suppose that all aging phenomena—i e , changes in physical properties (mechanical, electrical, magnetic) taking place near room temperature—should be caused by the same type of structural change in the material At the Westinghouse research laboratories we have devoted considerable time and effort to determining the actual changes involved, therefore I am much interested in Mr van Wert's paper, aside from the fact that I was instrumental in providing him with samples of iron for his investigation

In regard to the solubility of oxygen in alpha iron, my associate, Mr Ziegler, has found very slight variation in the solubility between 0° and 900°, the actual value being of the order of 0 01 per cent At about 950°, however, there is a decided jump, the solubility reaching a value of nearly 0 1 per cent Any iron that has been subjected to temperatures above 900° under atmospheric conditions consequently will contain in the neighborhood of 0 1 per cent oxygen, and it is doubtful whether the "pure" iron used by Mr van Wert contained much less than this amount This may account for the results obtained In order to get iron with 0 01 per cent oxygen or less, it is necessary either to forge it at a relatively low temperature or to add a small amount of carbon to the iron in the melting furnace, which can be removed subsequently in company with the oxygen as CO by annealing in vacuum A third alternative is to anneal in hydrogen at a high temperature

The results of Mr van Wert's experimental work are definite, and the conclusions seem logical The author finds a decided decrease in the blue-brittleness effect as the amount of impurities decreases, and vice versa, except in the case of Izett steel He concludes that the effect is due to impurities in supersaturated solution, the precipitation of which is facilitated by the mechanical straining, acting as "keys" to check further plastic deformation I suppose we may liken the phenomenon to the effect of a social disturbance, all available forces are called out to oppose it, whether it be for good or for bad

In addition to aging after overstrain and blue brittleness, we have long been familiar with the phenomenon of aging of permanent-magnet steel, the coercive force of which depends on the amount of carbon retained in solution by quenching from a high temperature Being supersaturated at room temperature there is always a tendency for the carbon to precipitate as Fe₃C and thus to lower the coercive force But how can this same explanation hold for magnetic aging of opposite sign of nearly pure iron, slowly cooled? We know that such iron sometimes ages considerably even at room temperature, the more so, the purer the iron In this case the coercive force increases with time and it seems logical to assume that impurities are going into solution from without Then, along comes Koster and describes aging of quenched Fe-N alloys; here the coercive force increases with time and is attributed to precipitation hardening We thus have the anomalous condition that in one case the coercive force is decreased by precipitation of impurities, in another case it is increased by assumed precipitation, and in a third case it is increased by impurities supposedly

going into solution   If we take for granted that these assumptions are correct—and there is good evidence in each case—we must conclude that the changes in physical properties depend not only on whether impurities go into solution or are precipitated, but in the latter case also on the type of precipitation taking place   A more general-ized statement in regard to aging, therefore, is that aging may be caused either by impurities precipitating from solution or by impurities entering into solution, and that the corresponding changes in the physical properties will depend on the relative *strain relations* in the lattice structure before and after the aging   I would like to suggest that this possibility be kept in mind in the further study of aging, particularly of nearly pure iron

R S DEAN, Washington, D C (written discussion[*]) —While I am in entire agree-ment with Mr van Wert's major premise, there are a few points I should like to men-tion   The explanation of blue brittleness as put forward by Mr Gregg, Mr Day and me was that the precipitated iron nitride went into solution with a combination of cold work and increased temperature   Blue brittleness was therefore solution hardening   Aging, on the other hand, was explained as dispersion hardening   While it is possible to explain the phenomena observed by a delayed precipitation accele-rated by cold work, the evidence is not yet available to distinguish between these two possibilities

There are two reasons why I prefer the solution hypothesis   The first is that a sample of iron containing nitrogen which has been put through a cycle of working and reheating, and which might therefore be assumed to have separated all the nitride, would still show blue brittleness, and the other is that the electrical resistance increases when hardening takes place in the blue-brittle range

The author's observation that, with enough nitrogen, blue brittleness may be lowered to 100m temperature is not in accord with our observations that the blue-brittle range was the same in wire containing 0 086 per cent nitrogen as in wire containing 0 007 per cent nitrogen   I should attribute his results rather to the quenching and consequent very fine state of the separated nitride, which made it go into solution more rapidly

Mr Mehl has suggested an experiment to distinguish between dispersion and solution hardening, which constitutes approaching the blue-brittle range from above in such a way that there can be no solution phenomenon   The results of such an experiment should be definitive, and I hope Mr Mehl will be able to carry it out in the near future

YAP, Chu-Phay, New York, N Y (written discussion) —In 1927 in my paper on grain growth in mild steels[28] I noted age-hardening effects and to account for them proposed a solid solubility line as shown in Fig 8   If anyone has previously proposed such a line, I am not aware of it, although I note that thereafter several diagrams have been published with the solubility line as shown [29]

Is solubility purely a function of temperature alone?   Hulett,[30] among others, has definitely proved that another factor that influences solubility is the free surface energy of the dispersed phase, that is, the finer the salt, the more soluble it should be

* Published by permission of the Director, U S Bureau of Mines

[28] Yap, C-P   On Grain Growth in Mild Steels   *Trans* Amer Soc Steel Treat (1927) **12**, 609.

[29] R   L   Dowdell   Phases of Metastable Iron-carbon Constitution Diagram *Metals & Alloys* (1930) **1**, 515   The author refers to diagrams by Grossmann, Yensen, Sato, Daeves and others in which the solubility line is shown

[30] J Alexander   Colloid Chemistry, 637   New York, 1926   Chemical Catalogue Co

The fundamental equation based on Lord Kelvin's thermodynamic equation as developed by Ostwald and later corrected by Freundlich is

$$\ln \frac{s_2}{s_1} = \frac{2M\sigma}{RT\rho}\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \qquad [1]$$

in which RT and M have the usual significance, s_2 and s_1 are the concentrations of the solution (in terms of the solute) in equilibrium with particles of radii r_2 and r_1 respectively, σ the surface energy and ρ the density of the solid

If the normal particle size is large, the surface would be planes and r_1 would be equal to ∞, so that $(1/r_\infty)$ cancels out, s_1 would then be the normal solubility, which we shall hereafter designate as s_∞ (Also, arithmetically, as long as r_1 is large compared to r_2, the term $1/r_1$ can be safely disregarded without appreciable error) Equation 1 then reduces simply to

$$\ln \frac{s_2}{s_\infty} = \frac{2M\sigma}{RT\rho r_2} \qquad [2]$$

or

$$\ln s_2 = \frac{2M\sigma}{RT\rho r} + \ln s_\infty \qquad [2a]$$

Equations 2 and 2a clearly show the relation between the normal solubility and supersolubility due to the influence of surface energy of the very fine particle size of the solute in equilibrium with the solution

If the value of σ is fairly large and the particle size is small, the state of supersaturation will be appreciable Thus, we can safely conclude that the solubility line shown in Fig 8 is variable depending upon the treatment and previous history of the steel sample Of course, the presence of another element alone may narrow or widen the field of solubility of Fe_3C From a study of the binary diagrams of Fe-O and Fe-C, I believe that oxygen would tend to narrow rather than to widen the field of solubility [30]

These remarks are taken from a paper now in course of preparation I merely wish to call attention to this subject, which I hope may help us to visualize the degree of supersaturation possible with solute of fine particle size as met with in quenched steels
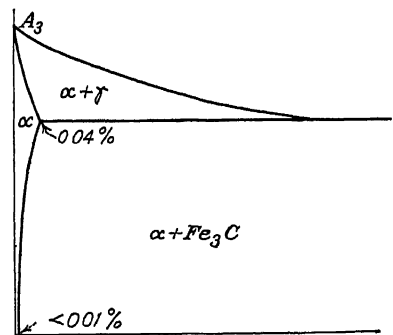
FIG 8 —SOLID SOLUBILITY OF CARBON OR CARBIDE IN FERRITE NOT DRAWN TO SCALE

H D HIBBARD, Plainfield, N J —The phenomenon of blue-heat brittleness of low-carbon steel reaches its maximum at the point of greatest tensility when the steel is heated, which is close to 290° C and not 300°, as intimated in the paper The tensility curve of such steel when heated slopes gently downward to a minimum at 100° C then rises somewhat abruptly to a maximum at 290° C then downward to a minimum at 800° C then rises to a maximum at 900° C and then slopes down to zero at about 1500° C The mention of Howard's temperature tests is interesting to me because I made the steel for them at the Norway Iron and Steel Works at South Boston, Massachusetts

A SAUVEUR, Cambridge, Mass —There is a great deal to be said in favor of the precipitation theory In our work at Harvard we have taken the appearance of the steplike form of curve in our twisting tests as an indication or proof of aging

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[30] I shall try not to complicate the problem by introducing the phenomenon of colloidal protection of the highly dispersed Fe_3C by the presence of FeO

With that in mind, we have investigated many alloys and whenever we have found a steplike curve we have inferred that the metal would age   Obviously, if aging is a precipitation theory, a pure metal should not age, but it is very difficult to obtain a chemically pure metal   The nearest approach was in the case of copper, and we found indeed that copper of great purity did not show a steplike curve, from which we inferred that pure copper does not age   I dare say if we obtained chemically pure iron, we would not find any steps in its curve   Steps occurred in Mr Yensen's iron but apparently because his iron contains a substantial amount of oxygen

In regard to the Izett steel which we subjected to a torsion test, it shows a slight indication of aging   The curve is not perfectly smooth, it is wavy   The steps are not present, in spite of the fact that Izett steel contains a substantial amount of oxygen   However, in talking about that matter with Dr Fry himself, I learned from him that while his steel contained a substantial amount of oxygen it was chiefly present as inclusions   He said that it is oxygen dissolved in the iron that causes aging   That is the way he explained that in spite of the presence of a substantial amount of oxygen in his steel the steel is free from aging and blue brittleness

In regard to the point made by Mr Hibbard that the blue-heat brittleness should occur at 290° and not at 300°, the difference is not great   Let us remember that it is affected by the speed of testing   With increased speed of testing the maximum point occurs at higher temperatures   So we cannot say that it is exactly 290° unless we have been told what the testing speed was, and again slight differences in chemical composition will have some effect also, I think, on the peak

The Austenite-pearlite Transformation and the Transition Constituents

BY ALBERT SAUVEUR,* CAMBRIDGE, MASS

(New York Meeting, February, 1931)

SOME writers believe that when austenite transforms completely into pearlite on slow cooling through the thermal critical range, such transformation does not imply the formation of any of the so-called transition constituents. martensite, troostite and sorbite   Might it not be claimed with as much justification that when water freezes it does so suddenly, solid ice being obtained without passing through the intermediate stages of ice and water?   Obviously, regardless of the speed of solidification, this would be erroneous.   Before reaching the completed solid condition, this must of necessity pass through an unbroken series of stages when the system consists of mixtures of water and of ice, the former decreasing and the latter increasing in amount.   Are not these "transition" stages in the freezing of water similar to the transition stages occurring in the transformation of austenite into pearlite?

To clarify, let us consider in Fig 1 the mechanism of the transformation of eutectoid steel from its austenitic to its pearlitic condition as it cools slowly through its thermal critical range   It is generally admitted that this transformation is the result of two distinct phenomena· (1) the allotropic change of gamma iron into alpha iron and (2) the crystallizing out of solution of the carbide Fe_3C Whether this crystallizing of Fe_3C implies also its formation is immaterial for our purpose   In other words, whether it is the carbon in atomic dispersion which is present in gamma iron or molecules of Fe_3C has no bearing upon the matter to be discussed   The transformation of gamma iron into alpha iron cannot take place suddenly   It must of necessity be progressive, regardless of the speed with which it may take place   At A, for instance, there would be present AB gamma iron and BC alpha iron   The distance MN does not refer to falling temperature, but to the passage of time   It may be assumed that the transformation takes place at a constant temperature (the Ar_{321} point)   In a similar way, the crystallization of Fe_3C out of the austenite solid solution must be progressive as depicted between M and N At A there would be present AB gamma iron, BC alpha iron, CD carbon dissolved in gamma and in alpha iron and DE Fe_3C This condition may be described according to individual preference as martensite or troostite   To sum up, can the metal pass from condition

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* Professor of Metallurgy, Harvard University.

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M to condition N without assuming the stages depicted between M and N, characterized by decreasing gamma iron and dissolved carbon and increasing alpha iron and Fe_3C, until finally at N the transformation is completed and pearlite is formed?

The claim that while a change of state must necessarily be progressive an allotropic transformation may take place so suddenly throughout the mass that transition stages (gamma-alpha mixtures) are nonexistent seems untenable   Indeed, the writer, in collaboration with Dr C H Chou, has shown the progressiveness of that transformation in pure iron [1]

FIG 1   FIG 2   FIG 3
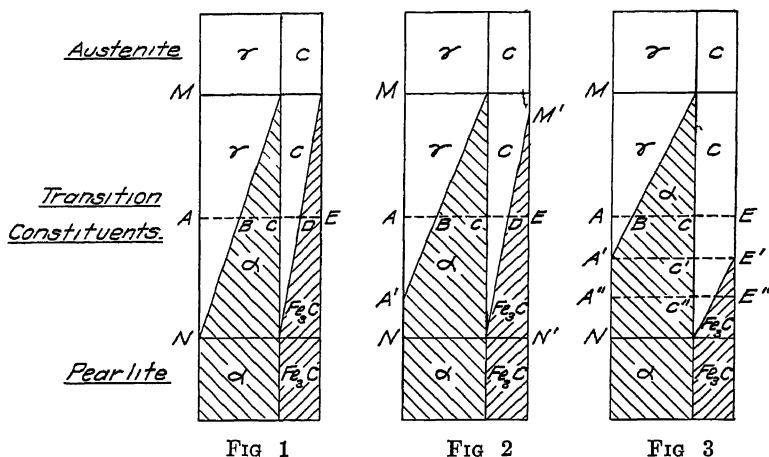
FIG 1 —MECHANISM OF TRANSFORMATION OF EUTECTOID STEEL FROM AUSTENITIC TO PEARLITIC CONDITION

FIG 2.—ALLOTROPIC GAMMA-ALPHA TRANSFORMATION BEFORE CRYSTALLIZATION OF CEMENTITE

FIG 3 —FORMATION OF CRYSTALLIZED CEMENTITE AFTER COMPLETION OF GAMMA-ALPHA TRANSFORMATION

It might be assumed on reasonable ground that the allotropic gamma-alpha transformation starts before and that it is completed before the crystallization of cementite, since the latter must result from the presence of alpha iron   This has been depicted in Fig 2   The allotropic transformation starts at M and is completed at A', while the cementite separation begins at M' and ends at N'.   At A we would have an aggregate of gamma iron and alpha iron containing some carbon in solution and of Fe_3C.   At A' no gamma iron would remain   Again, it might be conceived, although it seems unlikely, that the formation of crystallized cementite does not start until the gamma-alpha transformation has been completed   This has been depicted in Fig 3   At A there would be an aggregate of gamma and alpha iron containing carbon in solution, while at A' there would be a solid solution of carbon in alpha

[1] A Sauveur and C H Chou The Gamma-alpha Transformation in Pure Iron *Trans.* A I M E, Iron and Steel Div (1929) 350

iron, corresponding to what some consider to be the nature of martensite
At A'' an aggregate would exist consisting of a solid solution of carbon
in alpha iron and of cementite, claimed by some to be the composition
of troostite

These various hypotheses all call for the formation of transition
stages   Looking at the transformation of austenite in this light, we may
consider the nature of the transition stages   It is obvious that between
M and N an infinite number of transition stages exist, and we may
wonder whether we are justified in arbitrarily selecting certain types of
structure to be described as martensite, troostite, sorbite   What places
do these structures occupy in our illustrations?

In the writer's opinion, both so-called martensitic and troostitic
structures are aggregates of gamma and alpha iron containing carbon in
solution, and of the carbide Fe_3C corresponding to the transition stages
between M and N and, therefore, of indefinite composition   To draw
demarcation lines between them does not appear warranted   Sorbite
may be considered as a stage corresponding to the complete disappearance
of gamma iron and of dissolved carbon immediately preceding the
lamellar arrangement of these constituents in the formation of pearlite

The transformations that have been considered demand a certain
plasticity in order that they may proceed to a completion   This plas-
ticity exists at elevated temperature, but is absent at low temperatures
It is readily conceived, therefore, that any rate of cooling sufficiently
rapid to delay the transformation to considerably lower temperatures, as
in quenching, will prevent complete transformation at least, hence the
retention of some transition stage necessarily in the condition of an
unstable equilibrium

It is, of course quite possible, or even probable, that the transition
stage existing on slow cooling and corresponding to the composition of
martensite will not assume the same form as the constituent of the same
composition formed in quenching   In other words, it may well be that
an acicular structure does not form during the slow and complete trans-
formation of austenite.   This, however, would not justify the conclusion
that transition stages corresponding *in composition*, if not in structural
aspect, to martensite and troostite do not form when austenite transforms
to pearlite

In both cases we are concerned with the breaking up of the solid
solution austenite (1) slowly and completely at an elevated temperature,
or (2) quickly and incompletely at a low temperature   The new phase
separating from the solution—namely, alpha iron retaining some carbon
in solution—locates itself at some of the crystallographic planes of the
mother austenite, giving rise to the Widmanstatten type of structure on
slow cooling and to the martensitic type on rapid cooling   On slow
cooling, moreover, the carbon first retained in solution in alpha iron

crystallizes out and the alpha constituent converts into pearlite   On rapid cooling, on the contrary, some carbon is permanently retained in solution in the alpha phase   The mechanism of the formation of a Widmanstatten structure on slow cooling is the same as the mechanism of the formation of a martensitic structure at a low temperature

The transformation of austenite through the formation of the Widmanstatten structure is readily revealed in hypoeutectoid steel where ferrite (the alpha phase of first consolidation) is found to occupy certain crystallographic planes   In eutectoid steel no trace is left of the Widmanstatten structure as it existed at an early stage of the transformation, owing to the fact that the alloy is now completely pearlitic

Martensite is considered by many to be a solid solution of carbon in alpha iron and the "needles" of hardened steel described as consisting of martensite   Evidences seem to indicate, however, that the needles contain precipitated carbides and that they are, therefore, of the nature of troostite

Structure of Hardened Steel

The structure of hardened steel can best be described as representing an aggregate of residual (retained) austenite and of partly decomposed austenite (the martensitic needles), the latter consisting of alpha iron containing some carbon in solution and of precipitated carbide   The properties of hardened steel for a given composition should depend (1) upon the amount of retained austenite, and (2) upon the composition of the martensitic needles, that is, on the proportion of dissolved carbon and of precipitated carbon they contain   Obviously, the more drastic the cooling, the more carbon should be retained in solution in the alpha iron of the needles, while reheating hardened steel (tempering) should promote further transformation of the retained austenite and additional precipitation of carbides, that is, the formation of transition constituents corresponding in composition to troostite and martensite

Conclusion

These remarks are offered in the hope that they may stimulate discussion and criticism and thus throw more light on a phenomenon which is of fundamental importance in the metallographic study of iron-carbon alloys

DISCUSSION

(R F Harrington presiding)

A E Cameron, Edmonton, Alta (written discussion) —Dr Sauveur, as we have come to expect from him, has set down in simple understandable language thoughts which for many of us have been hovering around in the subconscious, scarcely clarified enough in our minds for concrete words   With simple diagrams and simple words

he puts forward theories that even the modern student, with his love for statements of fact and perhaps dislike for deductive reasoning, cannot help but trace to their logical conclusion

For some years I have attempted to show to my students that the terms martensite and troostite are not names for substances but rather for structures, representing, as Dr Sauveur has so clearly shown, "aggregates of gamma and alpha iron containing carbon in solution, and of the carbide Fe_3C" Sorbite I have generally placed in the same category, although I cannot agree with Dr Sauveur that "it may be considered as a stage corresponding to the complete disappearance of gamma iron and of dissolved carbon immediately preceding the lamellar arrangement of these constituents in the formation of pearlite" Undoubtedly there has been a complete disappearance of gamma iron and of dissolved carbon but it does not seem possible that the granular arrangement of cementite, so typical of sorbite, could develop and then the granules coalesce to form the platy or lamellar arrangement of pearlite

Lamellar pearlite, as we all know, on prolonged heating below the Ac_{3-1} point (divorce annealing) will granulate or coalesce to form granular pearlite In other words, the tendency at elevated temperatures is away from the platy type of structure, not towards it Sorbite, or rather the sorbitic structure, I have always interpreted as the coalescence or granulation of cementite which was previously precipitated or ejected from the gamma or alpha austenite The fineness or coarseness of the sorbitic structure depends upon the length of time allowed for granulation more than upon anything else

I am pleased to note Dr Sauveur's mention of the Widmanstatten type of structure developed in pearlite Perhaps this has been touched on elsewhere but I have not noted it before I would go further than he, and include martensitic structures as typically of the Widmanstatten type These seem to me to be true differentiation of two solid solutions The gamma-alpha transformation can begin most readily at two points—on the crystallographic planes of the austenite and at the grain boundaries On the crystallographic planes, particularly the (111) plane of the gamma iron lattice, the iron atoms are arranged to permit of minimum change in position to satisfy the alpha iron lattice, hence alpha iron (with or without carbon in solution) could form readily Conditions at the grain boundaries also are worthy of consideration Here we have iron atoms in a condition of restraint and without concentration Obviously any change in those conditions or release of restraint would permit of ready rearrangement to a stable form and one would expect new substances or phases to develop there early in the transformation

Martensite would be a typical Widmanstatten development of one solid solution on the crystallographic planes of another The new solid solution may be alpha austenite or it may be alpha iron If alpha austenite, the precipitation of cementite would develop the black or dark needles of martensite, the density of color depending upon the amount of carbon present in the steel and hence the amount of carbon or carbide retained in the alpha phase and subsequently precipitated If the new solid solution is alpha iron (ferrite), white needles result We all know that typical martensitic structure, particularly in low-carbon steels, shows both dark and light needles

Typical globular troostite, so well illustrated in Dr Sauveur's textbook, forms, for the most part, on the grain boundaries of the original austenite, in fact, I feel that such is its only position and the appearance of globules within an austenite grain is due to the plane of the polished surface cutting a section through a pendant globule from the upper or lower surface of the austenite grain Troostite appears to me to be definitely tied in with the grain boundary, and its development can best be explained as the result of the gamma-alpha transformation commencing in those regions It always etches dark and hence is a two-component aggregate Possibly there is carbon concentration within the amorphous cement or possibly there is
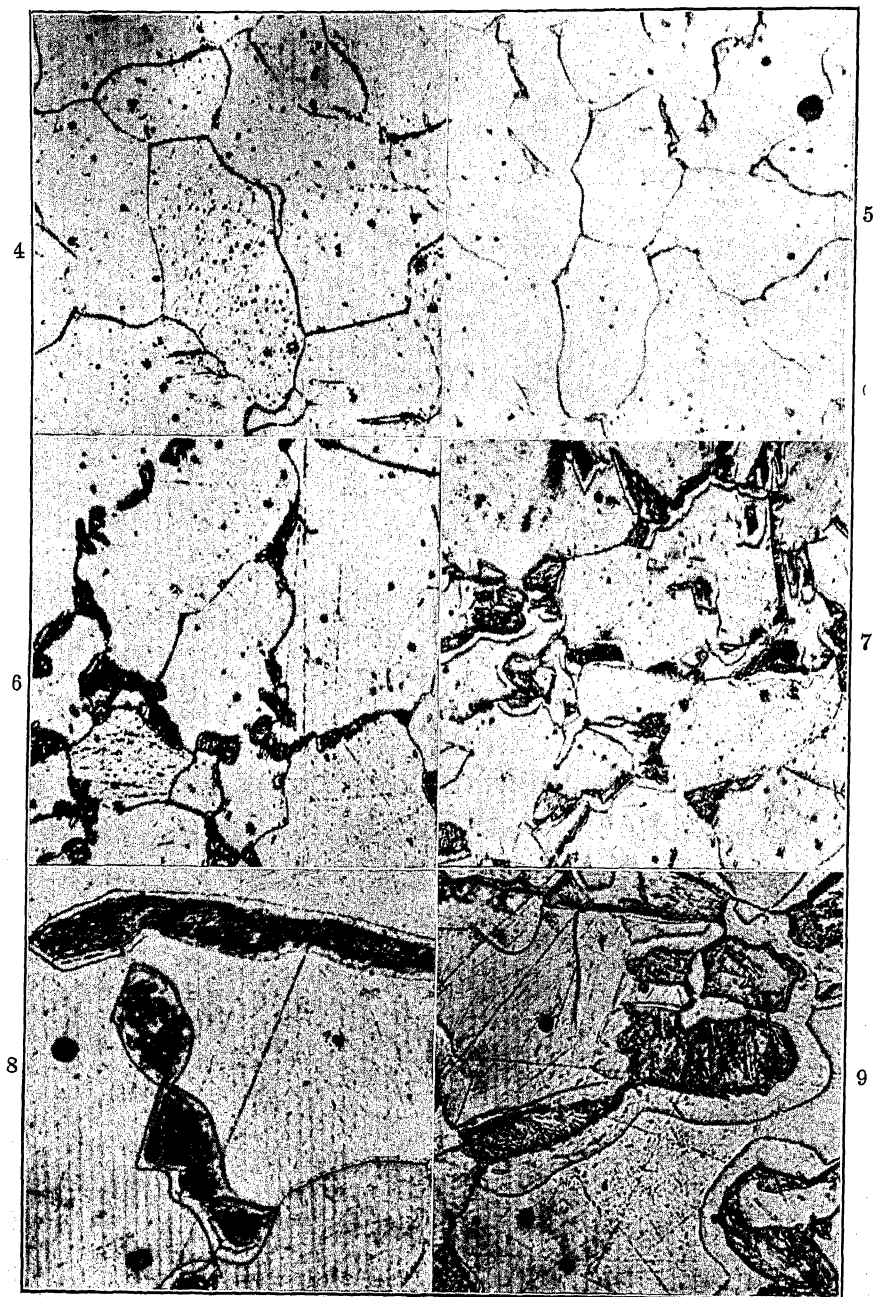
FIGS. 4–9.—COMMERCIAL INGOT IRON.

FIG. 4.—ANNEALED AT 1650° F.   × 300.   FIG. 7.—QUENCHED AT 1550° F.   × 300.
FIG. 5.—QUENCHED AT 1350° F.   × 300.   FIG. 8.—QUENCHED AT 1450° F.   × 1000.
FIG. 6.—QUENCHED AT 1450° F.   × 300.   FIG. 9.—QUENCHED AT 1550° F.   × 1000.

surface concentration of carbon in the individual austenite grains   These and the subsequent precipitation of carbides within the newly formed alpha austenite would account for the characteristic dark etching   On the other hand, an associate and I have shown, elsewhere,[2] that some typical globules of troostite on reheating fade in color and develop apparently to simple alpha iron (ferrite)   Hence there may be troostitic structures formed by aggregates of gamma and alpha iron without the presence of carbon, though quite conceivably some of the other ordinary constituents of steel may be responsible for the structure

The results of some recent work on commercial ingot iron are worth noting in this regard   Figs 4 to 7 illustrate approximately the same area of a piece of ingot iron after (1) annealing at 1650° F , (2) quenching from 1350° F , (3) quenching from 1450° F , (4) quenching from 1550° F   Note the production of troostite-like structures at the grain boundaries of the alpha iron   They are not troostite due to the presence of carbon but they must surely represent a multiple component aggregate and I believe they represent the incipient development of gamma iron or, in other words, the beginning of the alpha-gamma transformation   This change is most readily started at the grain boundaries where there are at least a few atoms not already oriented and hence ready to take on a definite orientation or attach themselves to a definite lattice when the conditions are such that the lattice on which neighboring atoms are arranged is unstable   Figs 8 and 9 show at high magnification portions of the areas covered by Figs 6 and 7   These structures are rather difficult to interpret and any suggestions on them would be welcomed

Troostite is usually considered a decomposition product of martensite   If by troostite we mean the typical globular structures we all know, this discussion emphasizes the fact that it is not a decomposition product of martensite but a primary decomposition product of austenite, and may be formed contemporaneously with martensite

I agree with Dr Sauveur that the "transition stages corresponding in composition if not in structural aspect develop during slow cooling to pearlite " We must, however, restrict such compositions to definite areas within the transforming mass, and this appears difficult to do inasmuch as only the final result is seen, and at that time migration, coalescence, segregation, etc , have distributed the products to very different locations and concentrations from those at which the structural nomenclature would apply   In other words, I do not think we should apply the well-known nomenclature to these corresponding composition stages   I realize that Dr Sauveur does not definitely advocate this either, though it could be inferred from his paper

A SAUVEUR (written discussion) —I note that Professor Cameron does not believe that sorbite corresponds to a stage in the transformation of austenite immediately preceding the formation of pearlite   It is true, as he says, that long reheating of pearlite slightly below its critical point (the spheroidizing treatment) causes the cementite plates to be converted into globules, resulting in a somewhat granular structure, but this phenomenon does not, in my mind, preclude the possible formation of a granulated form of pearlite (sorbite) preceding the occurrence of true pearlite through the coagulation of the cementite granules into plates   The cementite particles present in sorbite are divided much more finely than those occurring in spheroidized pearlite   They may border the colloidal stage

With Professor Cameron's belief that the martensitic structure is a sort of Widmanstatten structure, I fully agree, as will be apparent from three of my papers '

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[2] A E Cameron and I F Morrison Troostite   *Trans* Royal Society of Canada [3] (1928) **22**, Sec 3, 289

[3] A Sauveur The Widmanstattian Structure of Iron Alloys   Amer Phil Soc (1927) **66**, Austenite and its Decomposition Amer Soc Steel Treat (1929); and with C H Chou, The Gamma-alpha Transformation in Pure Iron   *Trans* A I M E , Iron and Steel Div. (1929)

In regard to the nature of the martensitic needles and of their formation, I find myself in close agreement with Professor Cameron   Noting his use of the expression "alpha austenite," by which he clearly means alpha iron retaining carbon in solid solution, it is to be feared that this might lead to some confusion, as the use of the term austenite has always been confined to solid solutions in which the solvent was gamma iron

As stated in the articles mentioned in footnote 3, I regard troostite as the alpha constituent separating from austenite as the latter transforms   This constituent, troostite, forms along crystallographic planes and at grain boundaries in the form of needles (so-called martensitic needles), later, if time be given, to be converted into a globular form (so-called globular troostite)   It is interesting to note that in Professor Cameron's opinion globular troostite would form for the most part at the grain boundaries of the austenite grains

I agree with Professor Cameron in his belief that the dark areas developed in commercial ingot iron on quenching indicate the beginning of the alpha-gamma transformation and are, therefore, of a troostitic nature   His statement that troostite is not a decomposition product of martensite but a primary decomposition product of austenite is welcome   It is in line with the opinion I have expressed on several occasions   I go a step further, however, as I consider troostite and martensite as fundamentally identical constituents

Age-hardening of Austenite

By F. R. Hensel,[*] East Pittsburgh, Pa

Up to the present time few attempts have been made to produce hard nonmagnetic materials by heat treatment of austenitic steels   The usual result has been to cause them to pass into the martensitic stage, thus destroying to a great extent the typical austenitic properties, since this involves a transition of a portion of the iron from a face-centered to a body-centered type of atomic arrangement

High-strength nonmagnetic materials such as might be provided by properly hardening austenite are required in the electrical industry for different machine parts   In Europe nonmagnetic retainer rings for restraining the end-turns of the rotor windings in turbo-alternators have been developed as a special application of high-strength austenite

In testing[1] a 28,000-kva three-phase Siemens turbogenerator running at 3000 r p m at full load current, the losses in the short-circuit test were 450 kw for the magnetic ring and 286 kw for the nonmagnetic, and the difference should be attributable to the magnetic ring   The differences in temperatures during the same test are given in Table 1 and these show the advantage of a nonmagnetic over a magnetic retainer ring

TABLE 1 —*Differences in Temperature*

Phase	Magnetic Ring, Deg C	Nonmagnetic Ring, Deg C
End plate outside	59	
End plate middle	73	33 5
End plate inside	83	39 5

Hardening in this case was obtained by cold working, such as hammering, rolling or some means for stretching the steel while at a temperature near 500° C   One means for stretching[2] is to rotate the forged or rolled ring in a centrifugal machine so as to develop within it stress higher than

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* Westinghouse Electric & Manufacturing Co

[1] G Koehler Ueber Stirnstreufelder und Zusatz verluste in Turbogeneratoren *Siemens Ztsch* (1926) **6**, 605–611

[2] Brit Patent 282015

its yield point Thus the ring is stretched and acquires a higher yield point in the direction of stretching

The material used for this purpose has about the following composition [3] carbon, 0 63 per cent , manganese, 8 75, nickel, 7 50, chromium, 3 40 After proper treatment such a steel will reach 100,000 lb per square inch yield point and still give 30 per cent elongation

This paper describes the results of an attempt to apply the precipitation or age-hardening method to austenitic steels [4] Age-hardening is the result of the precipitation of a certain metallic constituent from a saturated solid solution previously formed by proper heat treatment. The object was to find a high-strength material which after heat treatment combined high elastic properties and high elongation Another outcome of the precipitation-hardening method might be a material which would combine rust-resisting properties with maximum hardness Precipitation-hardening opens a new field for γ-iron metallurgy[5] and much research will be required to find out all the possibilities of this method

MATERIALS USED

Three types of austenitic steels are most frequently used in practice, namely, the 13 per cent manganese steel with 1 2 per cent carbon, the stainless steel containing 18 per cent chromium and 8 per cent nickel, and the 20 to 27 per cent nickel steel in which nickel may be replaced wholly or in part by manganese

It was decided to choose the nickel-manganese steels for these age-hardening experiments The base alloy used contained 15 per cent nickel, 10 per cent manganese and practically no carbon This composition gives a stable austenite and may be classified with the non-magnetic high-strength materials last mentioned above Titanium and molybdenum were added as age-hardeners in the forms of pure molybdenum powder and granular ferrotitanium The analysis of the latter was as follows titanium, 26 97 per cent , iron, 61 79, aluminum, 6 45, silicon, 2 48, manganese, 1 61, alumina, 0 92 The impurities, aluminum and silicon, must be taken into consideration because their amount increases with the titanium content of the alloys

Two series of alloys were prepared, one containing titanium, the other molybdenum in varying amounts All the alloys were melted in a high-

[3] D R Patent 298429

[4] P D Merica, R G Waltenburg and H Scott The Heat Treatment of Duralumin U S Bur Stds *Sci Paper* 347 (1919)

D Hanson and M L V Gayler The Constitution and Age-Hardening of the Alloys of Aluminum with Magnesium and Silicon *Jnl* Inst Met (1921) **26**, 321–355

W Rosenhain, S L Archbutt and D Hanson On Some Alloys of Aluminum (Light Alloys) Inst Mech Engrs , 11th Rept to Alloys Res Com (August, 1921)

[5] J A Mathews Austenite and Austenitic Steels *Trans* A I M E (1925) **71**,

frequency furnace in air atmosphere and cast in chill molds   The analyses are given in Tables 2 and 3

TABLE 2 —*Analysis of Titanium Alloys*

Mark	Ni, Per Cent	Mn, Per Cent	Ti, Per Cent	Si, Per Cent	Al, Per Cent	C, Per Cent	Weight of Ingot, Kg
2312	14 4	9 98					1
2372	14 77	10 35	1 86	0 35	0 22		1
2373	14 75	10 18	3 24	0 55	0 36		1
2374	14 4	10 08	4 49		0 66		1
2375	14 3	9 95	6 58	0 93	1 00		1
2376			10 0 added				1
2377			15 0 added				1
2378			20 0 added				1
2538	10 53	9 67	2 78	0 90	0 63	0 067	8
2539	12 67	9 66	3 96	0 62	0 78	0 10	8
2540	15 62	10 02	4 18	0 68	0 80	0 05	8
2541	15 37	9 94	4 15	0 73	0 68	0 06	8

TABLE 3 —*Analysis of Molybdenum Alloys*

Mark	Mo, Per Cent	Mn, Per Cent	Ni, Per Cent	Weight of Ingot, Kg
2355	1 83	10 01	14 78	1
2356	3 71	9 68	14 61	1
2357	5 54	9 36	14 38	1
2358	7 46	9 17	14 17	1
2359	8 98	8 82	13 96	1
2360	9 82	8 58	13 79	1
2429	13 50	8 87	13 07	1
2430	16 71	8 32	12 56	1
2431	20 68	7 82	12 06	1
2432	23 40	7 36	11 70	1
2665	15 42	8 22	13 95	8

FORGING CHARACTERISTICS

The titanium-bearing high-manganese alloys forged well up to 7 per cent Ti but with higher titanium content they became red short and broke up during forging.   The forging temperature had to be watched carefully, as the alloys are sensitive to overheating, 1000° to 1100° C was found to be the best forging range   Above 1250° C they become red short even with low titanium content

The microscopical analysis of alloy 2373 after quenching from different temperatures led to an explanation of this red shortness   The original structure as forged at 1000° C is seen in Fig 1   This structure was not changed after quenching from 1100° to 1200° C., but quenching
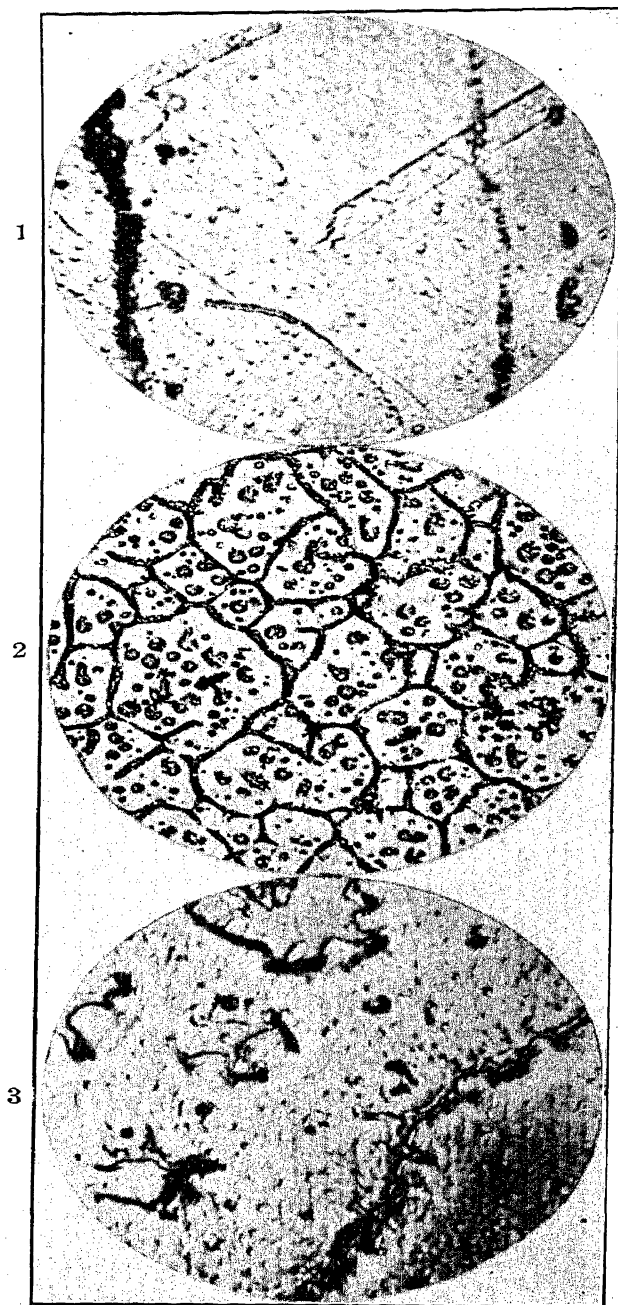
FIGS. 1–3.—AUSTENITIC TITANIUM ALLOY 2373.
1. As forged.   × 1500.
2. As quenched from above 1300° C.   × 100.
3. As quenched from above 1300° C.   × 1000.

from 1300° to 1350° C brought about the structure shown in Fig 2 at 100 dia and in Fig 3 at 1000 dia A new intercrystalline phase appears which, no doubt, is liquid above 1300° C and destroys the intercrystalline coherence of the materials at such temperatures Of interest are the hardness values of samples 2372 to 2375 after forging and quenching from 1200° C (Table 4)

All the molybdenum alloys forged well

TABLE 4 —*Hardness Values*

Mark	As Forged and Air-cooled, V P N [a]	Is Quenched from 1200° C , V P N
2372	150	128
2373	220	138
2374	265	160
2375	305	152

[a] Vickers Pyramid Numeral, so called because the Vickers machine uses a diamond penetrator in the form of a square pyramid with an obtuse angle at the apex The Vickers hardness is closely equivalent to Brinell in the present range of hardness The data were obtained by applying a load of 50 kg and using a 1½-in objective for measuring the impression

AGE-HARDENING EXPERIMENTS

Theoretical consideration led to the use of titanium and molybdenum as age-hardener

The iron-titanium equilibrium diagram[b] shows that solid iron dissolves only 6 3 per cent titanium The conditions in the solid state, especially the change of solubility with temperature, have not yet been determined, although this knowledge would be of great value in connection with further development of titanium alloys Alloys with 6 3 to 13 2 per cent titanium precipitate first the solid solution of 6 3 per cent titanium in iron and the solidification is completed by the formation of a eutectic with 13 2 per cent titanium at 1300° C Alloys with 13 2 to 22 3 per cent titanium precipitate first an intermetallic compound, probably Fe_3Ti, containing 22 3 per cent titanium The formation of a relatively low melting eutectic in the austenitic alloys as seen in Figs 2 and 3 was found to be the cause of red shortness above certain temperatures

Titanium decreases the magnetic properties of iron if added in considerable quantities Above 14 per cent titanium the magnetizability decreases rapidly and an alloy with 23 per cent titanium is practically nonmagnetic This fact led to the expectation of obtaining a stable form of austenite by adding titanium

[b] J Lamort Über Titaneisenlegierungen *Ferrum* (1913–14) 11, 225

The iron-molybdenum equilibrium diagram has been investigated lately by Sykes [7] According to his results molybdenum is soluble in solid iron up to 24 per cent The solubility decreases with the temperature from 24 per cent at 1440° C to 6 per cent at 400° C This reveals the possibility of producing age-hardening by means of molybdenum The best age-hardening temperature was found to be about 700° C , which produced a maximum hardness of over 700 Brinell At 36 per cent Mo a eutectic is formed consisting of the solid solution of 24 per cent Mo and the probable compound Fe_3Mo_2 containing 53 42 per cent molybdenum
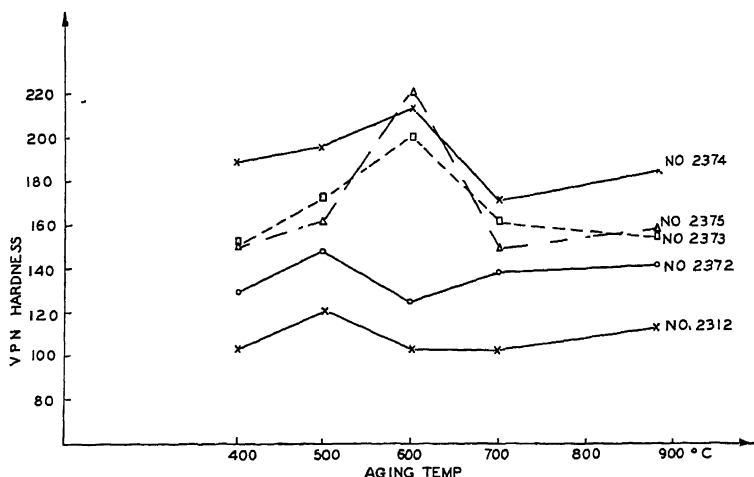
FIG 4 —AUSTENITIC TITANIUM ALLOYS WATER-QUENCHED FROM 1000° C , AGED FOR 1 HR AT DIFFERENT TEMPERATURES AND WATER-QUENCHED AGAIN

Similar conditions have been found in the iron-tungsten system, which also shows a change of solid solubility with temperature and has a range of alloys that can be age-hardened [8] Austenitic tungsten alloys, however, have not been included in the present investigation It may be expected that they will behave very much as do the molybdenum alloys.

Tempering-hardness Relations

The titanium alloy samples 2372 to 2375 were heated to 1000° C , water-quenched and aged for 1 hr at different temperatures in the range between 400° C and 900° C The samples were water-quenched after aging The results are plotted in Fig 4 There is a marked peak in the hardness values for the alloys 2373 to 2375 at 600° C and it was concluded that the highest hardness values would be obtained by aging at

[7] W P Sykes The Iron-Molybdenum System *Trans* Amer Soc Steel Treat (1926) **10**, 839–869

[8] W. P Sykes The Iron-tungsten System *Trans* A I M E (1926) **73**, 968

that temperature   The molybdenum alloy samples 2355 to 2360 (10 per cent Mo) did not show important aging effects   With higher molybdenum contents, as found in 2429 to 2432 (13 to 23 per cent Mo), aging proceeded rapidly at temperatures around 800° C , as can be seen from Fig 5   The samples were quenched from 1200° C and aged at various temperatures for 1½ hr   The hardness values reached range from 300 to 470 V P N   The hardness increase is about 100 per cent
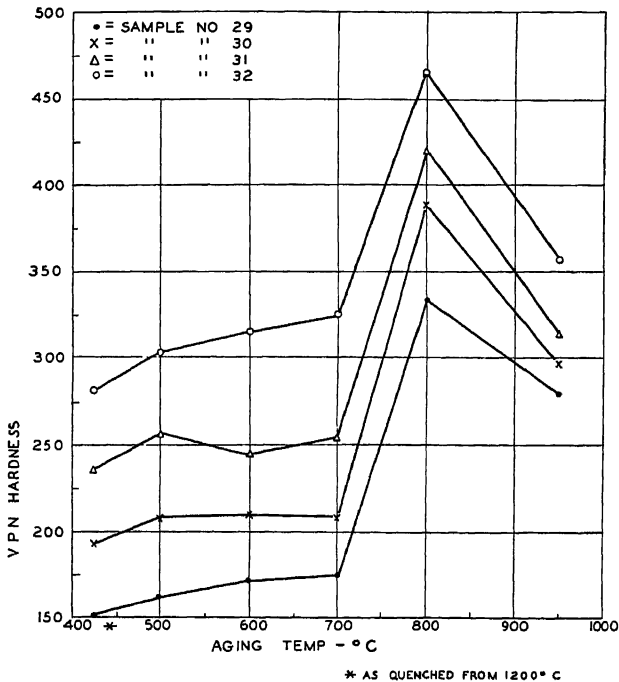
FIG 5 —AUSTENITIC MOLYBDENUM SAMPLES QUENCHED FROM 1200° C AND AGED AT VARIOUS TEMPERATURES FOR 1½ HOURS

Aging-hardness Relations

Aging experiments at 600° C show pronounced effects for the titanium alloys 2373 to 2375   Sample 2372 alone shows no aging   This seems to indicate that the smallest amount of titanium that will produce age-hardening properties is approximately 3 per cent   In some of the alloys the increase in hardness amounts to more than 100 per cent   Sample 2374 reached a hardness of 360 V P N after aging for 45 hr at 600° C. The curves are plotted in Fig 6

From Fig 7 it is evident that aging at temperatures either higher or lower than 600° C produces a lower hardness than that obtainable after aging at 600° C. Aging at 700° C did not increase the hardness to any appreciable amount

The time required to produce aging in the temperature range between 500° and 600° C is rather long—after 90 hr all the curves are still slightly rising   This probably means that these or similar alloys with titanium as age-hardener will prove useful for applications at elevated temperatures, since at 500° C it will take probably months to reach equilibrium It was found that heating to 1000° followed by air cooling, quenching or even furnace cooling did not greatly change the age-hardening properties   However, this may not be true of large pieces which cannot be so rapidly cooled

Two curves characteristic of the results obtained on the molybdenum samples 2429 to 2432 are shown in Figs 8 and 9   The temperatures
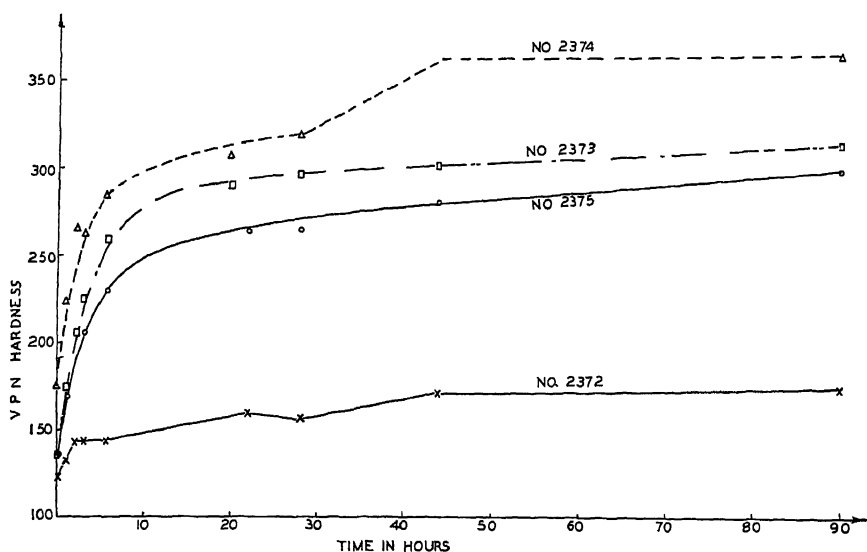
FIG 6 —AGING OF AUSTENITIC TITANIUM SAMPLES AT 600° C

750° C , 800° C and 850° C were chosen as aging temperatures   The samples were quenched in water from 1300° C before aging

With higher molybdenum content the actual hardness values are raised but the general trend of the curves is the same in all cases   The lowest aging temperature of 750° C gives the highest increase in hardness, while an aging temperature of 800° C gives somewhat lower hardness values and causes the hardness to pass through a maximum after a shorter aging time   At 850° C the hardness reaches a still lower maximum after 4 hr and then drops very rapidly

The mechanism of dispersion hardening, as shown by the results obtained, may be considered in connection with two factors which play an important part in the crystallization of undercooled liquids, namely, the number of nuclei and the velocity of crystallization   We undercool

a solid solution by quenching to temperatures low enough to prevent
relative movements of the atoms, and when we reheat, the formation of
an intermediate compound will start as soon as the atomic mobility has
been increased to such a point that the mechanical and chemical forces
are great enough to cause atomic and molecular rearrangements   There
is in most cases a fairly definite temperature below which such changes
cannot proceed   Above that temperature there exist for each aging
temperature certain values for the number of nuclei and the velocity of
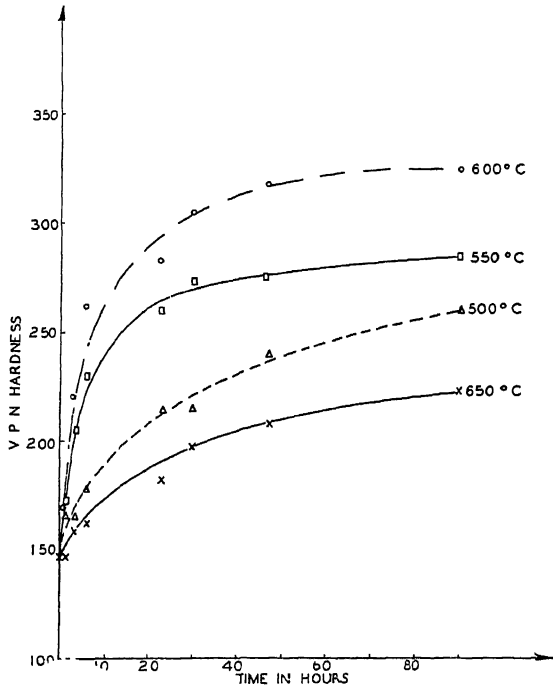
Fig 7 —Aging of austenitic titanium alloy 2373 at different temperatures
after water quench from 1000° C

crystallization which determine the size of the precipitated particles.
The number of nuclei usually increases with the degree of undercooling
and when the latter is great the tendency is toward the precipitation of
extremely fine particles   The velocity of crystal growth will increase
rapidly with aging temperature and beyond a certain point the particles
which were before submicroscopic become visible under the microscope
and tend to increase in size with time

   The increase in hardness is explained by assuming that the slip
planes of the original crystal and those of the precipitate are not parallel,
and that the precipitate thus blocks movement along the slip planes of

the original crystal   Rosenhain[9] explains the maximum hardening effect in aging as an equalization of an increasing hardness caused by precipita-
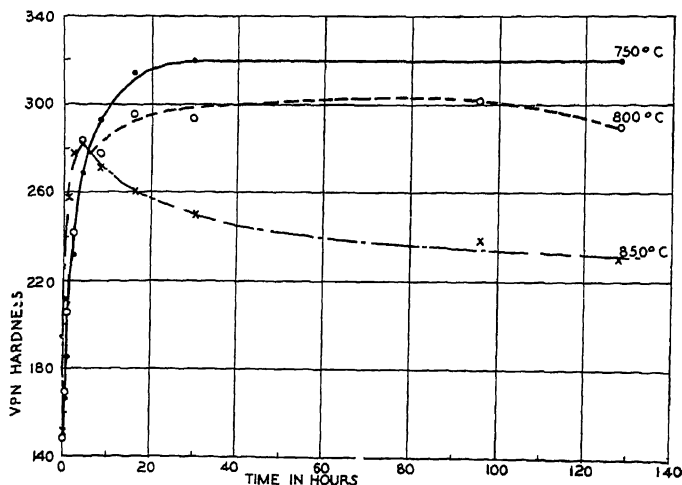
FIG 8 —AGING OF AUSTENITIC MOLYBDENUM SAMPLE 2429 AT VARIOUS TEMPERATURES AFTER QUENCHING FROM 1300° C

tion of new particles and a decreasing hardness resulting from coagulation of the already formed precipitate   Moreover, precipitation might
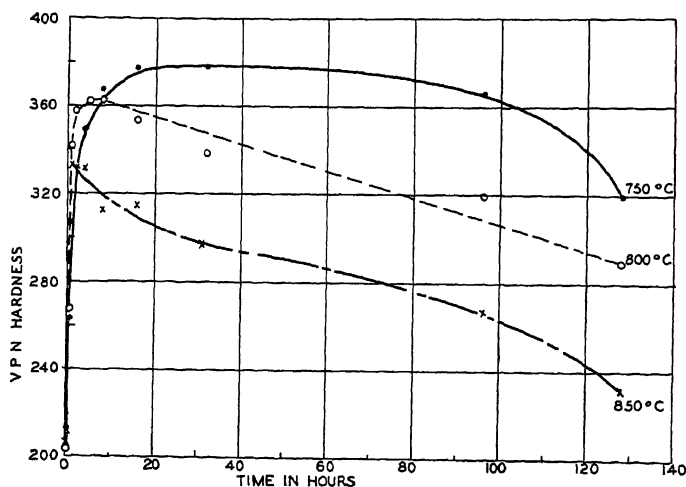
FIG 9 —AGING OF AUSTENITIC MOLYBDENUM SAMPLE 2430 AT VARIOUS TEMPERATURES AFTER QUENCHING FROM 1300° C

be accompanied by distortion of the atomic lattice, which would also cause increase in hardness

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[9] W Rosenhain Verguetbare Legierungen, Meinungsaustausch   *Ztsch f Metallk* (1930) **22**, 141–146

Alloys as Forged

Fig 1 showed a typical example of a titanium alloy (2373)   Streaks of yellowish, spherical or somewhat elongated particles stand out in relief   These particles are quite different from the groundmass in color and from the white spherical constituent which can be seen in Fig 10, probably they are a nitrogen-titanium compound   Titanium forms a number of nitrides, all of which resemble a light-colored bronze in appearance and are hard enough to scratch topaz, as for instance Ti_2N_2, Ti_3N_4 or a cyanonitride, Ti_3CN_4 Because of their low specific gravity (ranging from 4 1 to 5 2) it is expected that most of the titanium-nitrogen compounds formed would rise to the surface of the melt where they would be removed with the slag, thus leaving the metal free from nitrogen   It is evident that this did not happen in the experimental melts described here, but it should be possible to remove most of the nitrides by a suitable melting practice and thus obtain a material nearly free from nitrogen

The white globules are a titanium-rich constituent, both their size and number increase with the titanium content   They are found not only in the grains but along grain boundaries as well   After quenching from 1000° C many of these round particles remained undissolved

In the molybdenum alloys a secondary constituent appears in the austenitic groundmass and increases in quantity with increasing molybdenum content, as seen from Figs 11 to 13, taken at 1500 dia from sample 2356.   It seems to act as a kind of hardener of the austenitic matrix, as judged by the hardness values which are increasing with the molybdenum content. Above 20 per cent molybdenum, distinct austenitic grains can no longer be observed and the secondary constituent forms a large proportion of the whole mass   The melting points of the alloys are lowered considerably by adding molybdenum in quantities exceeding 15 per cent   This was demonstrated by a quenching experiment in which specimens were heated to above 1400° C   The alloys 2430 to 2432 melted while the others stood the temperature well

Alloys as Aged

The effect of the aging temperature was determined on some of the titanium alloys   After aging at 500° C the austenitic grains remained white upon etching, having a true austenitic appearance and showing twinning. Aging at 550° C produced a somewhat roughened groundmass but grain boundaries were still developed by etching   Treatment at 600° C destroyed the austenitic appearance   No grain boundaries were brought out by etching and the alloy had more the appearance of a continuous mass of a troostitic material as seen in Fig 14.   At 650° C
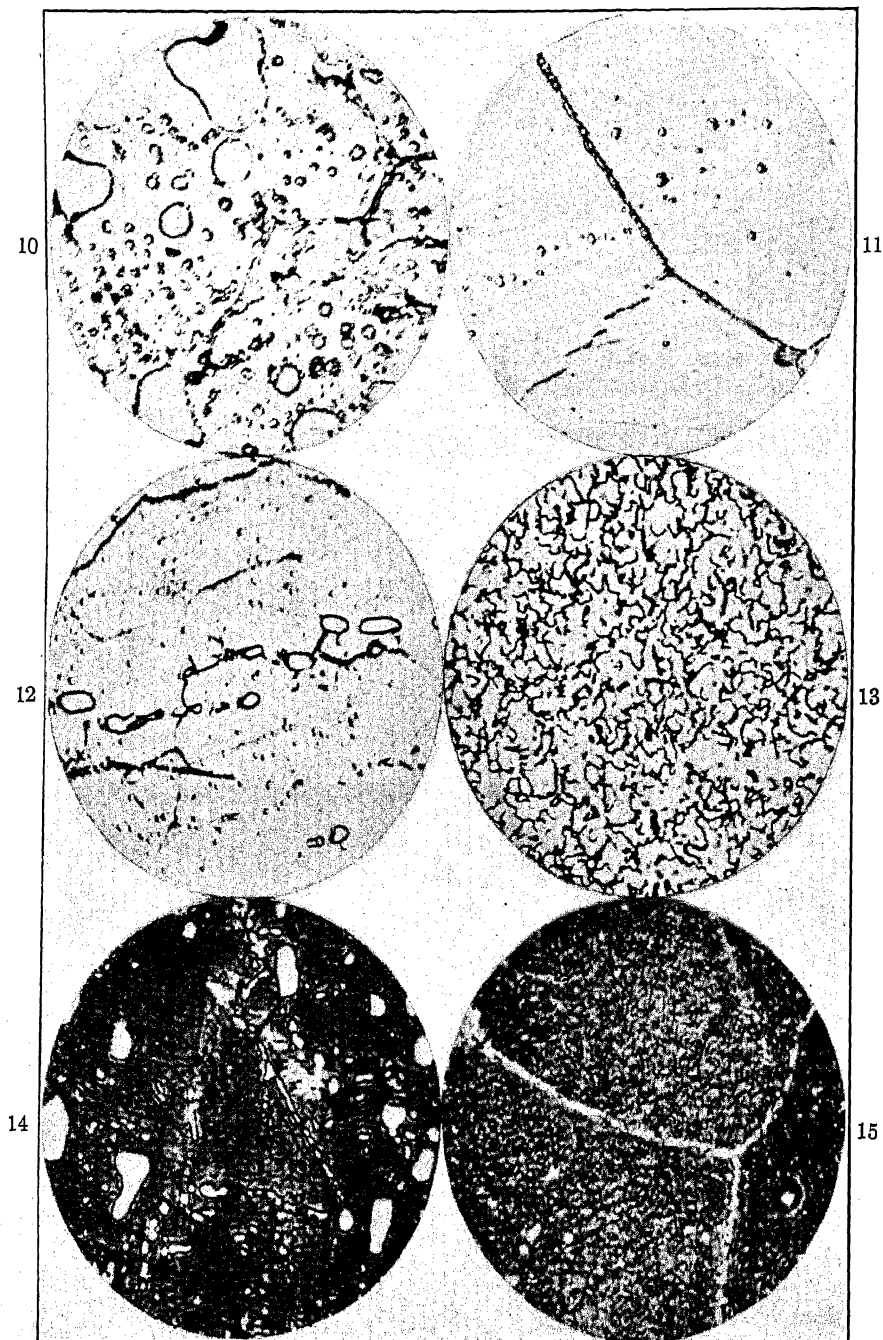
FIGS. 10–15.—CAPTIONS ON OPPOSITE PAGE.

a white constituent made its appearance along the grain boundaries and the hardness had begun to decrease. (See Fig. 15.)

X-ray Investigation

Titanium alloy samples 2373 and 2374 were prepared for X-ray analysis by rolling to 0.04-in. ribbon and etching it to still further reduce the thickness. The time of exposure was about 45 hr. The differences between the spectrograms were expected to be slight, therefore two samples were examined on each film in order to distinguish small differences. The lines in all samples represented the face-centered lattice of nonmagnetic γ iron. The lattice constant was 3.62. In each case two different aging treatments produced slightly different spectrograms; that is, the lines are shifted slightly by the aging treatments (Fig. 16).
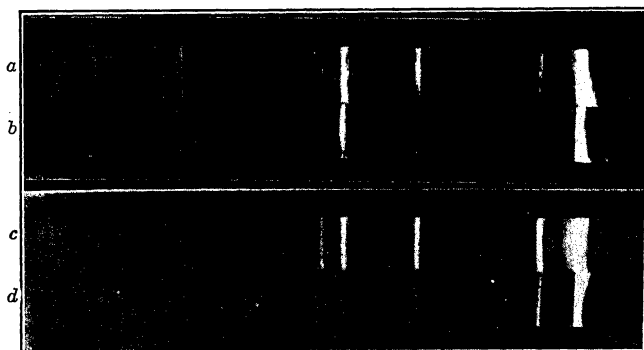
FIG. 16.—AUSTENITIC TITANIUM ALLOYS 2373 (a AND b) AND 2374 (c AND d).
a. Aged at 600° C. for 1 hr.   c. Aged at 600° C. for 40 hr.
b. Aged at 600° C. for 3 hr.   d. Quenched from 1000° C.

This means that a small change in the lattice constant has been produced, or in other words, a change in the composition of the solid solution. The lines of the precipitate are not clearly enough developed to permit the measurements necessary to identify the compounds producing them.

Volume Changes during Aging

The results obtained in measurements of specific gravity of the titanium samples 2373 and 2374 are recorded in Table 5. The relationship between hardness and specific gravity is seen from the curves of Fig. 17.

FIG. 10.—AUSTENITIC TITANIUM ALLOY 2375 AS FORGED.
FIG. 11.—AUSTENITIC MOLYBDENUM ALLOY 2356 AS FORGED.
FIG. 12.—AUSTENITIC MOLYBDENUM ALLOY 2358 AS FORGED.
FIG. 13.—AUSTENITIC MOLYBDENUM ALLOY 2432 AS FORGED.
FIG. 14.—AUSTENITIC TITANIUM ALLOY 2374 AGED FOR 3 HR. AT 600° C.
FIG. 15.—AUSTENITIC TITANIUM ALLOY 2373 AGED FOR 90 HR. AT 650° C.
ALL × 1500.

TABLE 5 —*Specific Gravity of Alloys*

Treatment	Specific Gravity	
	Alloy 2373	Alloy 2374
Heated in salt bath to 950° C , water-quenched	7 686	7 70
Aged for 2 hr at 600° C , in air	7 82	7 76
Aged for 9 hr at 600° C in hydrogen	7 85	7 77
Aged for 33 hr at 600° C in hydrogen	7 96	7 84

In both alloys, 2373 and 2374, the specific gravity increases during aging This is confirmed by the results of the expansion tests given below The test pieces for the expansion tests had the following dimensions. length, 4 02 in ± 0 005, ¼-in dia , ends = ⅛ radius   The apparatus was described by H Scott [10]
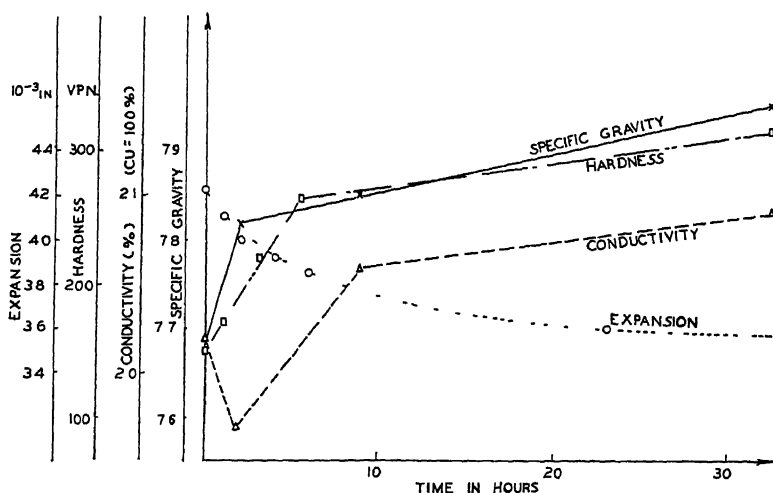
FIG 17 —CHANGE OF SOME PHYSICAL PROPERTIES OF AUSTENITIC TITANIUM ALLOY 2373 DURING AGING AT 600° C AFTER WATER QUENCH FROM 1000° C

For the first experiment, alloy 2373 was water-quenched from 1000° C and then put in the furnace, which was kept at 600° C and held at that temperature for 70 hr   The shrinkage during that time was 7 by 10^{-3} in or 0 18 per cent of the length   The rate of shrinkage decreased with the aging time and the curve assumed the shape of an asymptote to the time axis (Fig 17)

Fig 18 shows the expansion-temperature curve of alloy 2373 after quenching from 1000° C   It should be noted that at about 300° C the

[10] H Scott Expansion Characteristics of Low-expansion Nickel Steels *Trans* Amer Soc Steel Treat (1928) **13**, 829 Expansion Properties of Low-expansion Fe-Ni-Co Alloys *Trans* A I M E., Inst Met Div. (1930) 507

curve depaits fiom its previous iegular parabolic course This is an indication of the commencement of some moleculai change, piesumably the start of the precipitation piocess Above 600° C the curve again assumes a paiabolic shape Similar iesults weie obtained with the other titanium alloys The expansion-tempeiatuie curve is a good method for determining the progress of aging effects and ascertaining thei tem-perature limits for alloys which show volume changes duiing aging The method was not applied to the molybdenum alloys because the aging
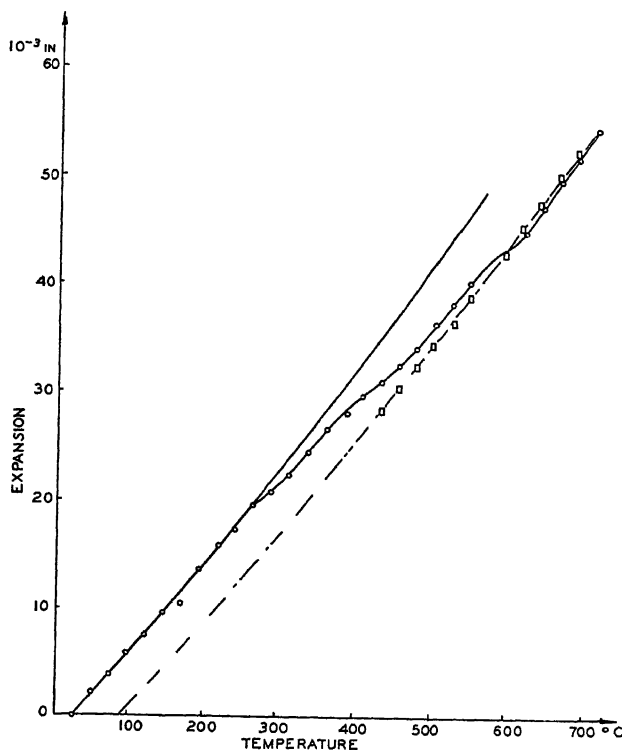
Fig 18 —Expansion-temperature relation of austenitic titanium alloy 2373 after quenching from 1000° C

temperatures are too high and it was not thought to be safe to run the apparatus to temperatures above 700° C Curves taken with the Cheve-nard thermal analyzer did not show these slight changes.

The shrinkage during aging is explained by assuming that the pre-cipitate is the result of the formation from the elements held in solid solution of compounds which are insoluble and whose crystals have much higher density than the original solid solution The volume change, therefore, can continue only as long as material is available for com-pound formation in excess of its solubility at the given temperature

Subsequently, when only the size and arrangement of the precipitated particles are being changed no irregularities of the expansion-temperature curve will be observed

The actual curve, therefore, is the resultant of two physical processes acting in opposite directions. (1) expansion as a function of temperature, (2) contraction as a function of molecular changes in the material   In heating the titanium alloys rapidly to 600° C the molecular changes do not affect the shape of the expansion curve very much   In holding at 600° C , however, these molecular changes become the determining factor of the course of the curve

It may be mentioned here that with increasing amounts of molybdenum the thermal expansivity decreases slightly

CHANGE OF ELECTRICAL CONDUCTIVITY DURING AGING

The results which have been obtained on titanium alloys are recorded in Table 6   Curves showing hardness and resistivity versus aging time are plotted in Fig 17

TABLE 6 —*Results on Titanium Alloys*

Sample	Heat Treatment	Resistivity, Ohms per Cu Cm	Conductivity, Per Cent of Copper at 25° C
2373-1	Quenched from 950° C	87 55	2 02
	Aged 2 hr at 600° C	88 16	1 97
	Aged 9 hr at 600° C	85 65	2 06
	Aged 33 hr at 600° C	83 1	2 09
2374-1	Quenched from 950° C	90 65	1 95
	Aged 2 hr at 600° C	91 2	1 92
	Aged 9 hr at 600° C	89 22	1 98
	Aged 33 hr at 600° C	87 25	2 00
2373-2	Quenched from 1000° C	87 3	2 01
	Aged 1 hr at 550° C	88 72	1 98
	Aged 2 hr at 550° C	88 6	1 98
	Aged 8 hr at 550° C	88 2	1 99
2373-3	Quenched from 1000° C	89 7	1 96
	Aged 1 hr at 600° C	89 5	1 96
	Aged 2 hr at 600° C	88 63	1 98
	Aged 8 hr at 600° C	88 4	1 99
2373-4	Quenched from 1000° C	89 3	1 96
	Aged 1 hr at 650° C	87 6	2 00
	Aged 2 hr at 650° C	87 6	2 00
	Aged 8 hr at 650° C	87 7	2 00

Owing to the low conductivity of the material, the percentage changes are small   More striking results in this respect are found in age-hardening copper alloys   The changes amounted to several hundred per cent for certain copper-titanium alloys investigated lately by the author

The samples 2373-1 and 2374-1 show an increase of resistivity in the first stages of aging and later a decrease   Aging of 2373-2 at 550° C decreases the conductivity first and increases it then very slowly   At 600° C no decrease occurs but the conductivity remains constant for about 1 hr. aging time and then increases   At 650° C the conductivity increases within a relatively short time after heating

According to the precipitation theory, there should be a steady decrease in resistivity together with an increase in hardness as the amount of material held in solid solution is decreased   For solid solutions we know that the resistivity increases rapidly as increasing amounts of one constituent are dissolved in the other pure constituent   Usually the resistivity of a solid solution is expressed as the sum of two parts (1) resistivity which can be calculated by means of the rule of mixtures from the resistance of the two pure metals, (2) an additional resistance due to the formation of a solid solution which in most cases seems to be but slightly dependent upon the temperature

According to Bridgman[11] the additional resistance is caused by the atoms of the element taken up in solid solution as they interrupt the undisturbed wandering of an electron from one atom to another   As aging proceeds it is possible that the first few new molecules formed act as would atoms of a new element in solid solution in an otherwise stable and homogeneous solvent, thus producing an initial increase in resistivity Fig 17 shows that the maximum hardness and minimum conductivity do not coincide   Masing[12] has tried to calculate the particle size that causes this disturbance in Cu-Be alloys

The anomalies of the electrical resistance have been lately explained by H Esser and W Eilender[13] as a function of the cold deformation which they assert is connected with the precipitation of small particles   The conductivity changes, according to their assumptions, result from (1) decrease of electrical resistivity due to precipitation from the solid solution, (2) increase of resistivity due to the cold deformation of the space lattice connected with the precipitation

The amount of the cold deformation is a function of the aging temperature, according to Esser and Eilender   This would explain the fact that at lower aging temperature we get an initial decrease of conductivity

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[11] P W Bridgman The Electric Resistance of Metals   *Phys Rev* (1924) **17**, 161

[12] G Masing Zur Theorie der Vergutungsvorgange auf Grund der Untersuchungen an Beryllium-Kupferlegierungen   *Wiss Veroff Siemens-Konz* (1929) **8**, 193

[13] H Esser and W Eilender Uber die Stahlhartung   Arch f Eisenhuettenw (1929–1930) **4**, 142–143

due to the preponderance of process 2 while at higher temperatures process 1 preponderates so much that the anomalies disappear

The explanation sounds reasonable if the assumption is justified that precipitation produces plastic flow similar to that produced by cold working   For steel in which hardening is accompanied by expansion, it might hold true, but for age-hardening alloys in which precipitation is connected with shrinkage it seems to be somewhat doubtful, it seems to be more reasonable to believe that upon quenching some cold working occurs which is released by aging, since the system then is allowed to get back to equilibrium conditions

CHANGE OF PERMEABILITY DURING AGING

From Table 7 it is evident that the changes in general are very slight and can be neglected for practical considerations   The permeability increases with the aging time at first but subsequently decreases if the aging time exceeds a certain limit   The permeability values after quenching from 1000° C for the molybdenum alloys 2356 to 2431 were below 1 01

TABLE 7 —*Permeability Changes in Sample* 2373

H Gauss	As Forged, μ	As Quenched from 1000° C, μ	As Aged, μ			
			1 Hr	3 Hr	14 Hr	100 Hr
50	1 84	1 53	1 55	1 80	2 33	1 79
100	1 79	1 53	1 55	1 67	1 96	1 66
200	1 60	1 39	1 43	1 51	1 66	1 51
300	1 49	1 30	1 34	1 39	1 53	1 44
500	1 36	1 22	1 26	1 29	1 37	1 33

PHYSICAL PROPERTIES IN THE QUENCHED AND AGED STATE

The results of the tensile tests of molybdenum and titanium austenitic steels after various heat treatments are collected in Tables 8, 9 and 10

Table 8 and Fig 19 show the tensile properties of the molybdenum alloys after quenching from 1000° C   Although many members of this series do not show aging, it was considered well worth while to determine first the influence of increasing amounts of molybdenum upon the physical properties of an austenitic matrix without applying age-hardening   The main result of these tests is that it was impossible to increase the proportional limit by adding molybdenum, although the yield point and tensile strength did increase with increasing molybdenum content   In general, the change in tensile strength resembles very much that of the hardness, although the hardness increases about 300 per cent while the corresponding increase in tensile strength amounts to less than 50 per cent   Above 10 per cent molybdenum a decided drop in ductility can be noticed.

TABLE 8 —*Tensile Properties of Molybdenum Alloys after Quenching from 1000° C*

Mark	Mo, Per Cent	Proportional Limit, Lb per Sq In	Yield Point, Lb per Sq In (0 2 Per Cent Plastic Strain)	Tensile Strength, Lb per Sq In	Extension, Per Cent	Reduction in Area, Per Cent	Hardness, VPN	Remarks
2355	1 83						110	
		22,400	41,500	90,800	49 5	66	110	
2356	3 71	22,400	43,400	93,000	58 0	68		
2357	5 54	28,400	51,500	101,800	37 0	58	135	Test section of all test
		19,600	55,000	101,600	38 5	62		pieces was 0 250 in
2358	7 46	18,400	41,800	96,000	42 8	57	145	dia with 1-in gage
		20,400	51,600	100,800	39 8	65		length
2359	8 98	26,700	56,000	104,500	37 2	58	145	
		20,400	56,000	104,600		58		
2360	9 82	20,400	50,500	102,600	42 5	54	160	
		26,500	54,800	103,000	35 7	48		
2429	13 50	17,150	53,200	121,000	27 0	28	250	
		21,200	63,200	135,000	21 8	26		
2430	16 71	18,550	61,200	127,800	21 3	24	310	
		20,400	69,100	143,000	10 9	16		
2431	20 68	20,400	69,500	133,000	7 8	13	320	
		19,400	66,300	126,600	4 2	6		
2432	23 40	22,400	88,300	139,000	0		350	Fractured in test piece threads
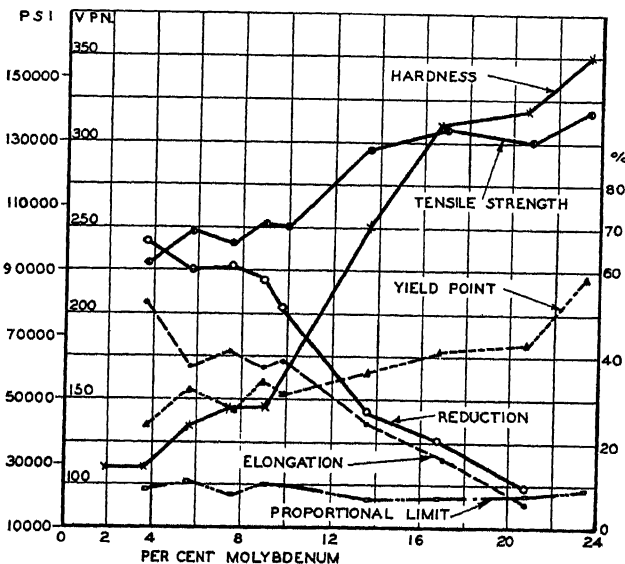
FIG 19 —RELATION BETWEEN TENSILE PROPERTIES AND MOLYBDENUM CONTENT OF
HICKEL-MANGANESE AUSTENITIC STEEL AFTER QUENCNING FROM 1000° C,

Table 9 and Fig 20 show test results for a 15 per cent molybdenum alloy after quenching and aging   Although there is an increase of Brinell hardness of 100 per cent , the increase in tensile strength does not amount to more than 30 to 40 per cent and the ductility decreases at

TABLE 9 —*Tensile Test Results of Molybdenum Alloy 2665 (15 42 Per Cent Mo) after Aging*

Treatment	Proportional Limit, Lb per Sq In	Yield Point, Lb per Sq In	Tensile Strength, Lb per Sq In	Reduction in Area, Per Cent	Extension, Per Cent	Brinell Hardness
As quenched from 1200° C	25,000	43,700	94,500	51 1	50 4	163
Aged 20 hr at 750° C	15,000	72,000	126,500	3 8	2 2	321
	14,000	75,000	126,700	Bk outs gage	1	321
Aged 30 hr at 750° C	16,500	70,000	129,000	5 1	2 8	321

TABLE 10 —*Tensile Test Results of Titanium Alloys after Aging*

Mark	Treatment	Proportional Limit, Lb per Sq In	Yield Point, Lb per Sq In	Tensile Strength, Lb per Sq In	Reduction in Area, Per Cent	Extension, Per Cent	Brinell Hardness
2528	Quench from 1000° C	22,000	41,250	85,500	46 9	44 6	
	Aged 65 hr 600° C	26,000	67,000	110,500	28 5	24 2	228
	Aged 112 hr 600° C	32,500	69,750	115,000	26 5	23 7	228
2539	Quench from 1000° C	15,750	37,375	86,500	43 7	36 5	174
	Aged 120 hr 600° C	25,000	92,500	125,500	8 5	5 9	293
	Aged 280 hr 600° C	45,000	93,500	105,000	3 5	2 9	Forging crack
2540	Quench from 1000° C	20,000	39,500	90,500	40 7	34 9	174
	Aged 50 hr 600° C	61,250	102,500	150,250	10 8	8 2	321
	Aged 120 hr 600° C	60,000	102,000	132,000	7 8	6 2	321
	Aged 280 hr 600° C	61,000	106,000	150,000	8 9	9 0	331
2541	Quench from 1000° C	16,500	45,000	89,250	35 4	33 0	166
	Aged 50 hr 600° C	56,000	101,750	139,750	5 9	4 5	321
	Aged 120 hr 600° C	70,000	107,000	156,500	13 8	13 5	331
	Aged 280 hr 600° C.	45,000	111,000	158,750	11 5	10 2	341

the same time from 50 to less than 5 per cent.   The increase in yield point is accompanied by a considerable lowering of the proportional limit In general, the tensile properties have not changed favorably during aging.   The results are somewhat similar to those obtained on iron-beryllium alloys.[14]   Ternary iron-nickel-beryllium alloys with 5 to 22 per cent nickel and 1 per cent beryllium show an extremely large increase in hardness with no corresponding increase in tensile strength, and a

[14] W. Kroll: Die Legierungen des Berylliums mit Eisen. *Wiss Veroff Siemens-Konz* (1929–30) 8, 220.
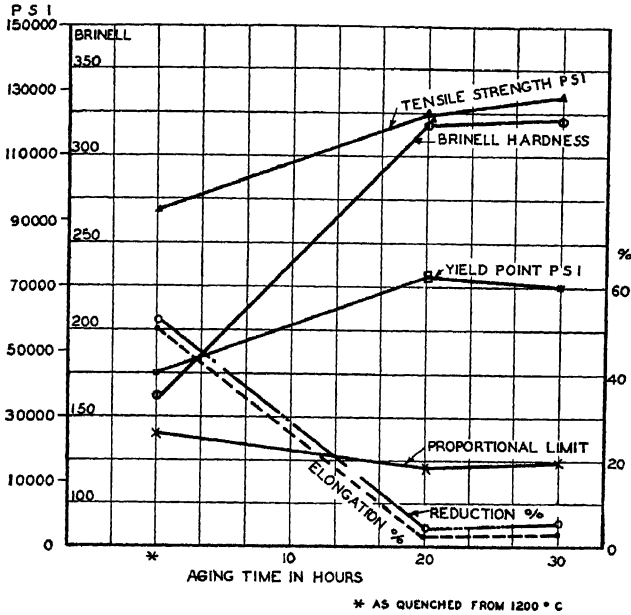
FIG 20 —CHANGE OF TENSILE PROPERTIES OF AUSTENITIC MOLYBDENUM ALLOY 2665
DURING AGING AT 750° C.
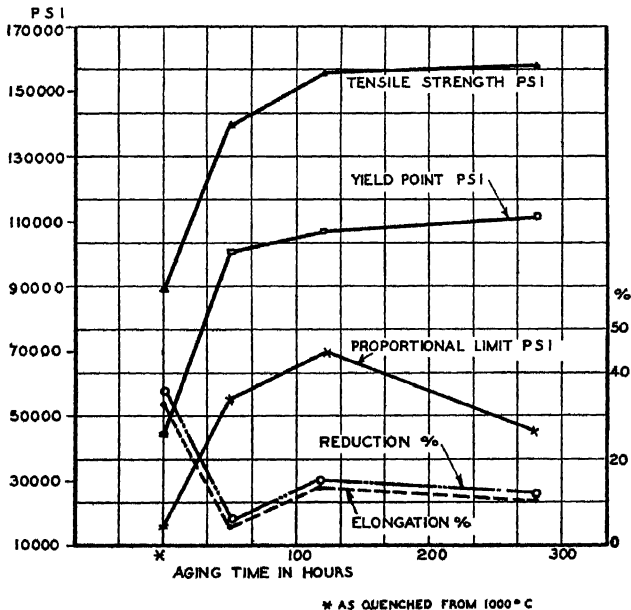
FIG 21.—CHANGE OF TENSILE PROPERTIES OF AUSTENITIC TITANIUM ALLOY 2541
DURING AGING AT 600° C.

drop of ductility to less than 5 per cent , and in many cases to less than 1 per cent elongation. Alloys of this type are not suitable for high-strength materials but they might be used for tools, springs and cutlery

Table 10 and Fig 21 show results of the tensile tests of titanium alloys after quenching and aging A fairly large increase in ultimate strength and a still greater increase in yield point is noticeable The latter is raised from 45,000 to 111,000 lb per square inch for alloy 2541 The increase in proportional limit from 20,000 to 70,000 lb per square inch is remarkable, too, for an austenitic material Unfortunately, the increase in tensile strength is connected with a very material loss of ductility, although the drop in elongation of the alloys 2540 and 2541 is much less pronounced than in the molybdenum alloys The object of further research on heat-treating of austenite therefore should be to produce an improvement of the ductility This can be done by changing either the matrix, the age-hardener or the heat treatment.

Very interesting data were obtained on two tensile test pieces machined from a ⅜-in round forged bar of titanium alloy 2373. The diameter of the test section was 0.250 in , the gage length was 1 in. The results were as follows:

Treatment	Proportional Limit, Lb per Sq In	Yield Point, Lb per Sq In	Tensile Strength, Lb per Sq In	Extension, Per Cent	Reduction in Area, Per Cent	Brinell Hardness
Quenched at 1000° C	14,250	29,100	83,700	26 8	72	129
Aged for 30 hr just below 600° C	22,400	68,500	142,400	40 0	52	237

These results have not been repeated and are given here with reservation as to their accuracy They seem to indicate, however, that there are ways of increasing the ductility of austenitic steels containing titanium.

By aging some of the titanium alloys at 550° C. instead of 600° C , a lower hardness is obtained but the ductility is increased considerably, as indicated in Table 11

TABLE 11.—*Tensile Test Results of Titanium Alloy 2539 after Aging at Different Temperatures*

Treatment	Proportional Limit, Lb per Sq In	Yield Point, Lb per Sq In	Tensile Strength, Lb per Sq In	Reduction in Area, Per Cent	Extension, Per Cent	Brinell Hardness
Quench from 1000° C	15,750	37,375	86,500	43 7	36 5	174
Aged 50 hr at 550° C	28,750	68,750	125,000	21 3	21 7	255
Aged 100 hr at 550° C	25,750	73,500	112,570	19 9	17 5	262
Aged 120 hr. at 600° C	25,000	92,500	125,500	8 5	5 9	293

Even better results can be expected with alloys of the type of No 2540 or No 2541, which have a higher nickel content and were more easily forgeable   Some of the poor results obtained on No 2539 undoubtedly are due to cracks developed during forging

CONCLUSIONS

1 The experiments have shown that the addition of 3 to 5 per cent. titanium or molybdenum above 13 per cent to a nickel-manganese austenitic base alloy makes it possible to obtain marked precipitation-hardening

2 Both the titanium and molybdenum age-hardened austenitic alloys remained nonmagnetic throughout heat and mechanical treatments.

3 Aging was accompanied in the titanium series by pronounced shrinkage, amounting in one case to approximately 0 18 per_ cent in length

4 The electrical resistivity of titanium alloys showed an abnormal change in that it first increased and then decreased

5 After aging at 600° C to maximum hardness, the titanium alloys presented a troostitic appearance

6. The X-ray analysis of titanium alloys showed that the lattice constant changed during aging .

7 The tensile and elastic properties of the titanium alloys were increased considerably by the precipitation-hardening   In one case the elastic limit was raised from 16,500 to 70,000 lb per square inch, with a yield point of about 107,000 lb per square inch.   Although this increase is connected with a material loss of ductility, the final value of the latter (13 5 per cent elongation) is high enough to make the material interesting from the engineering standpoint

8 The ductility of the titanium alloys was increased in one case from 5 9 to 21 7 per cent by aging at 550° C. instead of at 600° C.   Lower aging temperatures therefore give the best tensile properties with such alloys

9. The changes of the tensile properties of the molybdenum series during aging are not favorable   The elastic limit is lowered and the alloys lose their ductility nearly completely without corresponding increase in ultimate strength.

DISCUSSION

(Norman B Pilling presiding)

R. WASMUHT, Essen, Germany (written discussion) —The investigations described by Mr Hensel are highly interesting and form a valuable contribution to the metallurgy of γ iron   They show that just the γ iron is eminently suited to being age-hardened, a fact which technically may become highly important   It would make it possible to harden γ iron by heat treatment maintaining it in the γ phase   In this connection it must be appreciated that Hensel has also made X-ray investigations and proved by them that the γ phase of the examined steels was also maintained in the age-hardened state

In my research work at the laboratories of Fried. Krupp A G., Essen, I have obtained very similar results,[15] preferably using for my investigations the well-known stainless austenitic steels containing 18 per cent Cr and 8 per cent Ni   As age-hardener I used at first titanium, like Hensel, and afterwards boron   In the titanium-alloyed steels a considerable hardening effect was obtained with titanium contents lower than 3 per cent, as illustrated by Fig 15 for an 18 8 steel containing 2 3 per cent titanium   The most suitable aging temperature was 500° C , giving, for instance, an increase in hardness from about 300 to about 480 Brinell   These steels, it is true, are no longer entirely austenitic on account of their high titanium content, in contrast with the steels investigated by Hensel   The situation is different with the steels containing boron as age-hardener   These are austenitic even in the age-hardened state   Additions of a little more than 0 5 per cent B are sufficient to considerably raise hardness, tensile strength and yield point   An aging temperature of 700° to 800° C has been found to be most suitable   Fig 16, which is taken from reports not yet published, shows that the hardness of 18 8 Cr-Ni steels can be increased from about 250 to about 450 Brinell by the addition of boron and a suitable heat treatment   Precipitation-hardening also yields fairly high figures in the tensile test combined with a favorable relation between tensile strength and yield point Thus, for instance, an 18 8 Cr-Ni steel containing 0 55 per cent B gave after precipitation-hardening 126 kg per sq mm tensile strength and over 100 kg per sq mm yield point!

FIG 15 —TEMPERING ISOTHERMS OF 18 8 CR-NI STEEL CONTAINING 23 PER CENT TI AFTER QUENCHING IN WATER AT 1250°

N. B. PILLING, Bayonne, N J. (written discussion) —It is evident that rather closely parallel developments have been in progress recently dealing with means of improving the mechanical properties of austenitic steels and that several of these

[15] R Wasmuht   A Contribution to the Problem of Precipitation Hardening of Iron   *Met a All* **(1930)** **1**, 732, *Archiv f d Eisenhuttenwesen* (1929–30) **3**, 659, Die Ausscheidungshartung des Eisens durch Titan. *Archiv f d Eisenhuttenwesen* (1931–32) **5**, 45

investigations—those by Dr Kroll[16] at Luxembourg, by the Krupp company[17] at Essen, the Westinghouse company at Pittsburgh and the International Nickel Co at New York—have independently found and cultivated almost identical ways of accomplishing it   As is only to be expected, the degree of isolation existing between these groups is reflected in the varying ways in which the problem has been approached and in the details developed   It has been only a matter of time before means would be found to apply the principles of precipitation-hardening to the improvement of this class of iron alloy   Contrary to what might have been expected, the alloying elements suitable for accomplishing this effectively are limited in number, and all four researches seem to have found greatest promise in the element titanium
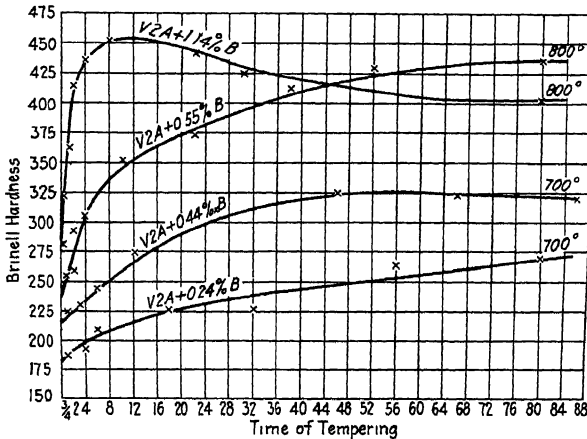
FIG 16 —DEPENDENCE OF PRECIPITATION HARDENING OF 18 8 CR-NI STEEL (V24 = STEEL) ON BORON CONTENT

The papers by Austin and Halliwell[18] and by Hensel are in a way supplementary to each other and between them disclose a number of suggestive characteristics brought out by the application of this kind of hardening to two special types of austenitic alloy, that is, nickel-manganese and nickel-cobalt steels   These facts should be of the greatest interest to those concerned with the possibilities of austenitic steels and should be of assistance in their further development

It is, however, possible to go somewhat farther than the authors have done and point out, first, the wide range of alloys which respond more or less similarly when provided with a suitable content of titanium and appropriately heat-treated, and second, the type of alloy which may perhaps prove to have more than transient interest to engineers

A number of circumstances suggest that it is titanium in association with nickel that constitutes at least one form of the hardening precipitate; the suggestion by Austin and Halliwell[19] that cobalt and iron appear to be essential may thus require some modification, and in fact the types of base composition which have been found responsive to titanium (although under conditions not necessarily always identical) include iron-nickel alloys, iron-nickel-chromium, nickel-chromium and nickel-copper,

16 See British Patent application
17 R Wasmuht Archiv f d Eisenhuttenwesen (1931).
18 C R Austin and G. P Halliwell. Some Developments in High-temperature Alloys in the Nickel-cobalt-iron System   A I M E   Tech Pub 430 (1931).
19 C R Austin and G P Halliwell Op cit, 21

as well as many derivatives of these Among these, tensile properties have been developed at room temperatures including proportional limits as high as 110,000 lb per sq in coupled with an elongation of 16 per cent, and apparent proportional limits, as developed under conditions of rather rapid loading, up to 80,000 lb per sq in at 550° C It is possible to state that the formidably long heat treatments extending through several days which both papers indicate can be greatly simplified and that the severe losses of ductility which were often encountered can be largely avoided

The nickel-chromium-iron alloys constitute a group which is unquestionably of wider intrinsic engineering interest than the cobalt and manganese alloys discussed by the present authors The fact that titanium becomes associated with nickel in the hardening precipitate assumes importance in attempts to improve such marginally austenitic alloys as 18 chromium, 8 nickel The resultant withdrawal of nickel from solution throws such a composition into the martensitic field, and the hardness thus developed, often fairly high, does not persist to very high temperatures As an example of the application of precipitation-hardening to an austenitic nickel-chromium steel, may I quote a few data relating to the following composition Ni, 15 5 per cent, Cr, 12 4, Ti, 2 70, Mn, 0 94, Si, 0 74, C, 0 16

Large ingots of this were forged to blooms, which in turn were hot-rolled to ⅞-in dia rod on a commercial mill Tension tests at room temperature on standard 2 by 0 505-in test specimens developed these properties

	Hot Rolled	Heat Treated
Proportional limit, lb per sq in	30,000	79,000
Yield point, lb per sq in	47,500	94,700
Ultimate, lb per sq in	96,100	157,000
Elongation, per cent	45 5	40 0
Reduction, per cent	62 1	56 3
Brinell	145	280
Izod	96	35

It is probably true that most of the uses to which high-strength austenitic steels might be put are limited to rather special cases in which, however important they may be to the application, no considerable tonnage of material would be involved A possible exception deals with a certain type of alloy for service at moderately high temperatures, particularly in the temperature range experienced in the operation of steam-power plants These high-strength alloys are at present only curiosities of the laboratory Indeed, so great is the task involved in development to the point of assured availability that those who would feel a responsibility in this matter may well pause at this point, and suggest to engineers who would ultimately be called on to use them to consider the limitations which it is already obvious these new alloys inherently possess, and indicate the extent of their interest There is now available a sufficient body of data to permit this preliminary appraisal

The principal limitations to which these alloys are subject have to do with the production difficulties resulting from the high reactivity of titanium, and the rather sharply defined temperature range within which the strength advantage exists The upper limiting temperature to which high elastic strength persists is certainly no higher than the precipitation range, at the most 1100° F. Above this temperature, loss of strength is rapid and even a short exposure dissolves the strengthening precipitate so that a temporary loss of strength occurs, which may persist at lower temperatures if subsequent exposure is at a temperature unfavorable for reprecipitation This danger must be clearly recognized, and obviously limits use to conditions where

unmanageable temperature fluctuations cannot possibly occur, as perhaps in steam engineering The comparatively low temperature limit thus imposed suggests a low-chromium content steel perhaps not greatly different in type from the example cited above Structural stability under long exposure to temperature, the magnitude and permanency of safe loading stress at high temperatures and many another question which may be put as to the dependability of these materials and the certainty with which they could be supplied, are questions which require long and expensive study But will the mechanical engineers first tell us how badly they are wanted?

F B FOLEY, Philadelphia, Pa —I was about to ask Mr Hensel whether or not he had determined the effect of aluminum in the compositions which he studied of his titanium-bearing steels, but that is very well explained in the paper by Austin and Halliwell

The reason for my questioning is that recently I have been playing with the use of nickel and aluminum in precipitation-hardening of ferritic steels I find that nickel and aluminum apparently are completely soluble in austenite, so that aluminum itself, added to an austenitic nickel steel, is not a source of precipitation-hardening

As Mr Pilling says, it would be interesting to find out what compound, if there is a compound, causes the precipitation when titanium is added My method of approach to that problem in connection with the steels with which I was playing was to eliminate one at a time various elements which might be concerned in the precipitation I finally got down to a steel which, if you could call it a steel, had carbon 0 03, nickel about 4 per cent, and aluminum about 2 per cent That underwent considerable precipitation-hardening When quenched from 1400° it was soft When reheated to about 1000°, it increased in hardness by perhaps 150 Brinell points When the nickel was removed there was no precipitation-hardening

With the carbon at 0 03, I felt there was very little precipitation from carbon If there was any it was very small indeed, as shown in some of the papers we recently have seen concerning the effect of small amounts of carbon on increasing the hardness of mild steels

H O'NEILL, Manchester, England —I have not had the opportunity to study this paper in detail, but a rapid glance through it convinces one of its practical and theoretical importance

In England, as Dr Hensel mentions, nickel-manganese steels are being used for generator end rings, and they prove to be very sensitive to forging The author's attempt to obtain hardened alloys by adding other elements to induce age-hardening is an interesting application of metallographic principles to a practical requirement. From the theoretical aspect some of the data are also valuable The figures for electrical conductivity, for instance, showing that curious fall at the beginning, will have to be taken into account in considering all theories of age-hardening. To some metallurgists the behavior of the conductivity property creates difficulties in supporting the precipitation theory of age-hardening, and the accumulation of data such as those obtained here will help in the building up and establishment of the final theory

I was rather surprised that the magnetic properties were considered to show no particular changes during aging I would like to ask the author whether values for coercive force, for instance, were obtained Perhaps one may be permitted to mention here the free-lance work which is being conducted in England by an engineer, E G. Herbert He obtains most curious results from various alloys, whether they be body-centered cubic or face-centered cubic, by giving them a magnetic treatment. For instance, Mr Herbert finds that if you quench a steel and measure its hardness at once you get a certain value, which after aging for a time is considerably increased. Then if you apply a magnetic treatment such as he prescribes—a very simple matter;

rotate the specimen in a uniform magnetic field—the hardening may increase very much more By repeating these magnetic treatments, results have been obtained showing that the hardening can be increased to a considerable extent Quenched duralumin, when subjected to this magnetic treatment, appears to age-harden more quickly than if it is allowed to stand at room temperatures [20]

If Mr Herbert thus finds that magnetism may affect age-hardening, one might have expected, conversely, that age-hardening would affect the magnetic properties

The elongation values for the quenched and for the aged alloys reported on page 276 certainly seem to be exceptional, for age-hardening has there caused a considerable increase in the extension One wonders whether the 26 8 per cent value for the quenched alloy is low for some reason or other

From the metallographic point of view I would like to ask whether most of these particular alloys give mechanical twins readily During polishing does one produce surface twins on the austenitic specimen, and if a sample be cold-worked—as by screwing up in a vise, for instance—does the structure then show mechanical twins?

F B FOLEY —I mentioned the fact that I did not think nickel and aluminum as a compound would precipitate from austenite and produce hardening My reasons for thinking so are these

As chromium was added to these nickel-aluminum steels, a high-temperature quench rendered them austenitic and practically nonmagnetic The Brinell hardness was about 200 When such specimens were heated to 1000° F —which was about the temperature of precipitation from the alpha iron—nothing occurred The hardness of the bars was still 207, 205, and they were still nonmagnetic When they were heated to about 1300°, the hardness rose to the neighborhood of 350 Brinell, and the specimens became magnetic If those specimens—magnetic and 350 Brinell—were reheated to 1000°, their hardness was increased further to about 450 Brinell

I concluded that the NiAl constituent was soluble in the austenite, certainly up to the limit of its stability in alpha iron under reheating I don't know whether with a completely stable austenitic alloy there is not some higher temperature at which the NiAl might precipitate, but I think it is extremely doubtful

F R HENSEL —With regard to the influence of nickel on the age-hardening of titanium alloys, I think that some light has been thrown upon this particular question by Dr Wasmuht in Germany As we all know, the age-hardening depends on the shape of the equilibrium diagram, and the iron-titanium diagram was only recently investigated to the eutectic temperature of 1300° C

The decrease of solubility in the solid state has been investigated recently by Dr Wasmuht The report was published in the July issue of the *Kruppsche Monatschefte* He shows that the solubility of titanium decreases with the temperature I think the solubility at the eutectic temperature is about 6 3 per cent titanium I have just glanced over his paper and I think he got age-hardening phenomena as low as 3 0 per cent titanium, so that the solubility at room temperature must be below that figure

In the next paper we will show that titanium in copper alloys has a similar effect That means its solubility decreases considerably from 900° to room temperature. At 900° C it is about 4 or 5 per cent, decreasing to 0 5 per cent at room temperature It is rather difficult to state which compounds fall out and cause precipitation-hardening effects

With regard to the other remarks, especially the remarks by Dr O'Neill, I think it is very important to study the theoretical side of the age-hardening phenomena with regard to the abnormalities of the electrical conductivity which we obtain in most of these systems

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[20] *Proc* Roy Soc (1931) A130

I studied only nickel-manganese alloys, having only a certain amount of time for this particular problem, and I thought it would be well worth while publishing these results in order to stimulate the application of this precipitation-hardening method for similar alloys

As Mr Pilling mentioned, Dr Kroll, in Germany, has applied precipitation-hardening by means of Be to non-nickel alloys, but as far as I am aware, his alloys showed only about 5 per cent maximum elongation after treatment, and quite a number of them did not give more than 1 per cent elongation, although they showed hardness as high as 600 Brinell

For high-strength austenite such alloys are certainly not suitable, although they may be applied to other purposes.

In regard to the twinning which Dr O'Neill asked about, I can say only that the austenitic appearance and the twinning disappeared more or less completely in the age-hardened alloys

Dr O'Neill mentioned the influence of age-hardening on the coercive force   In the austenitic alloys I did not investigate that point because as long as I had the permeability as near one as possible, I was satisfied, but we had another series of age-hardening alloys where age-hardening was caused by the presence of nitrogen   We find there that the coercive force is a good indication, probably the best indication, of aging phenomena

The coercive force or the maximum magnetic hardness and the maximum mechanical hardness are not obtained at the same particle size   We find, for instance, that where we get the maximum hardness in these alloys at room temperature, at which the precipitate is submicroscopic, we do not get any appreciable increase in the coercive force

However, aging iron-nitrogen alloys at 100° C where the precipitated particles can be seen under the microscope, we get a marked increase in coercive force, which confirms Dr O'Neill's statement that coercive force is a good indication of the changes that take place in the solid solution during precipitation-hardening

Transformational Characteristics of Iron-manganese Alloys

By Howard Scott,* East Pittsburgh, Pa

MANGANESE being perhaps the least expensive of the metallic alloying elements that can be advantageously added to iron in considerable quantities, the basic characteristics of its alloys with iron are properly receiving much attention at present   In the course of a dilatometric investigation of this system several years ago, the writer observed certain transformation phenomena not found in other iron-base alloys   The interpretation of those effects was not evident from the information then available, but recent X-ray studies clear up at least one anomaly and permit a more satisfactory description of the results than would have been possible otherwise

Aside from the new phenomena observed, the effect of manganese on the Ar_3 transformation is of timely interest because of its bearing on the critical compositions of austenitic alloys, the applications of which are now being greatly extended   It is known that the properties of these alloys are unstable unless the Ar_3 transformation occurs at a temperature considerably below atmospheric and that manganese is very effective in depressing the temperature of this transformation. The writer aims to establish a simple general relation which expresses the location of Ar_3 quantitatively in terms of the content of the common alloying elements used in steel.   A step in that direction is taken here

Early dilatometric investigations[1] indicated that only one transformation other than the eutectoid A_1 occurs in the high-iron alloys of the iron-manganese system.   Dejean represents the Ar_3 point as falling to 0° C. with a manganese content of 11 per cent and carbon content of between 0 30 and 0 40 per cent.   Esser and Oberhoffer,[2] using alloys low in carbon (under 0 03 per cent), arrived by extrapolation at 14 per cent for the manganese content at which Ar_3 is depressed to 0° C.   Not until both low carbon contents and alloys having a manganese content

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[1] P. Dejean· Des Aciers Auto-trempants et la Formation de la Troostite et de la Martensite   Rev de Mét (1917) 14, 641

[2] H. Esser and P Oberhoffer Zur Kenntnis der binaren Systeme Eisen-Silizium, Eisen-Phosphor und Eisen-Mangan Ver. Deut Eisenhuttenleute Werkstoff Ber 69 (1925).

around 14 per cent were used did the new transformation appear.[3] This transformation is of particular interest because it occurs with an increase in volume on heating in contrast with the volume change accompanying Ac_3

In other respects also the low-carbon iron-manganese alloys are unusual   At intermediate compositions, three different crystal forms
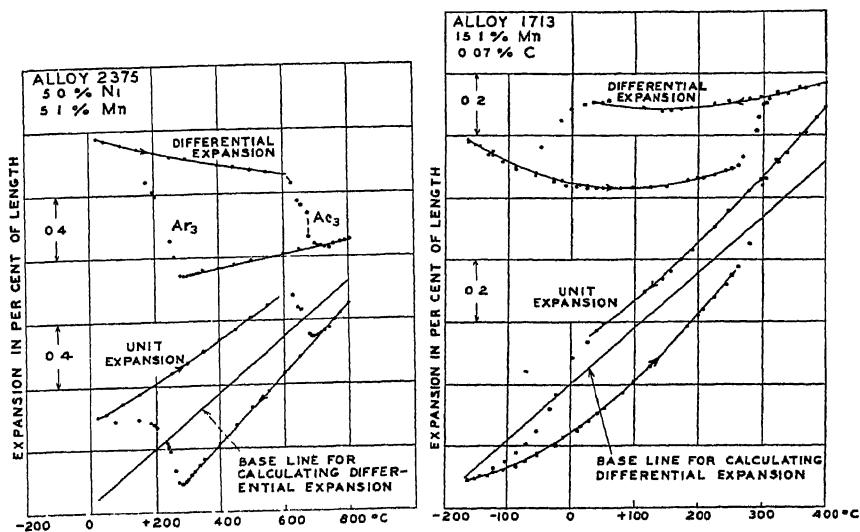
FIG 1 —DIFFERENTIAL EXPANSION CURVE OF FE-NI-MN ALLOY, SHOWING A_3 TRANSFORMATION COMPARED WITH UNIT EXPANSION CURVE

FIG 2.—DIFFERENTIAL AND UNIT EXPANSION CURVES OF AN FE-MN ALLOY, SHOWING TRANSFORMATION ACCOMPANIED BY INCREASE IN VOLUME ON HEATING.

appear to exist simultaneously in stable relations at room temperatures At high manganese contents there is found an abrupt increase in expansivity with increasing temperature, which resembles the Curie point or inflection temperature of the Invar type iron-nickel alloys except as regards loss of magnetizability.   It is the purpose of this paper to illustrate and give a brief description of these and other phenomena found in low-carbon iron-manganese alloys

IDENTIFICATION OF TRANSFORMATIONS

When the object of dilatometric observations is to reveal irreversible transformations by the accompanying length change, as in the present paper, it is advantageous to plot differential expansion rather than the total expansion.   That permits conservation of space and, more important, produces sharper contrast between the irreversible and the reversible length changes provided that the comparison standard is chosen so that

[3] T Ishiwara· On the Equilibrium Diagrams of the Aluminum-manganese, Copper-manganese and Iron-manganese Systems   Sci. Rept. Tohoku Imp Univ. [1] (1930) **19**, 499

the reversible portions of the curves are nearly flat, as in Fig 1   This is particularly true in regard to the new transformation, Fig 2   All of the curves are plotted in that manner

The expansion test method has already been described [4]   It is simply a differential method employing fused silica as the comparison standard The expansivity of silica is so low, however, that to use the differential method of plotting to advantage an artificial difference must be applied That is done by subtracting from the observed expansion per unit length the value obtained by multiplying the corresponding temperature in degrees Centigrade by the constant $17\ 5 \times 10^{-6}$ Consequently an approximate value of the coefficient of expansion of an alloy at a particu-

TABLE 1 —*Composition of Fe-Mn Alloys*

Alloy No	Mn, Per Cent	C, Per Cent	Si, Per Cent	Ni, Per Cent	L, Per Cent
2375	5 11	0 045	0 14	5 02	18 6
2374	5 10	0 054	0 13		13 7
1726	6 48	0 09	0 21		17 8
2373	7 48	0 082	0 18		20 2
1727	9 05	0 09	0 26		24 2
1694	11 3	0 16	0 12		31 1
1746	12 7	0 05			32 6
1695	13 7	0 075	0 19		35 6
1713	15 1	0 07			39 0
1728	16 93	0 17	0 58		45 4
1740	18 2	0 12	0 24		47 7
1739	19 8	0 11	0 26		51 0
2469	19 06	0 22	0 54		
1715	14 25	0 96			
2318	23 69	0 18	0 49		

Ferromanganese $= 1\ 8$ per cent Si, $0\ 03$ Al, $0\ 12$ C, $1\ 5$ Fe.   Per cent $L =$ per cent Ni $+ 2\ 5$ (per cent Mn) $+ 18$ (per cent C).

lar temperature can be had by adding $17\ 5 \times 10^{-6}$ per degree Centigrade to the value of the slope of the differential expansion curve at that temperature

Over certain temperature ranges the expansion is reversible; that is, the same on cooling as on heating.   To identify such temperature ranges, the plotted values within them are connected by a solid curve   The observations taken during an irreversible expansion are connected by a broken line or left unconnected, so that irreversible transformations may be easily recognized.

The alloys used were prepared from electrolytic iron and carbon-free ferromanganese by melting in a high-frequency induction furnace.

[4] H Scott Expansion Characteristics of Low-expansion Nickel Steels *Trans.* Amer Soc Steel Treat (1928) 13, 829

Atmospheric conditions are such that the pick-up of oxygen and probably of nitrogen is small The compositions of the alloys and of the ferromanganese by analysis are given in Table 1 Loss of manganese was uniformly 10 per cent of the charge The melts were cast in chill molds and in most cases forged to $^3_8$ in round, then swaged hot to $^1_4$-in dia for expansion test
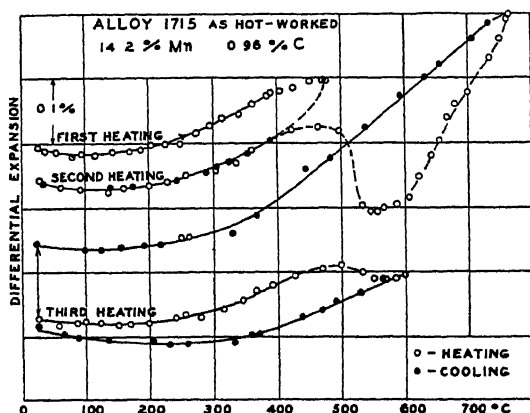
FIG 3 —DILATOMETRIC CURVES OF A HIGH-CARBON AUSTENITIC FE-MN ALLOY

To provide a background for the interpretation of the curves, another type of irreversible transformation is shown in Fig 3 The alloy tested was a high-carbon alloy of the type of Hadfield manganese steel, cooled in air from the forging temperature The permanent contraction on the first heating to 480° C is caused by the precipitation of carbides from solid solution. On the second heating a minimum permanent contraction occurs at about 550° C. and the carbon in solid solution is then a minimum. Continuing the heating to 765° C. caused re-solution of a considerable amount of the free carbide, which precipitated again on heating to 600° C., third heating.

The foregoing dilatometric observations enable one to recognize the phenomenon of carbide precipitation even if the carbon content is much lower than 1 per

FIG 4—DILATATION CURVE SHOWING THE EFFECT OF RATE OF COOLING ON THE PROGRESS OF THE AR₃ TRANSFORMATION

cent. Also, they illustrate a useful means for studying precipitation hardening The temperature of the minimum on the differential expansion curve is an important basic characteristic of a precipitation

hardening alloy because it is indicative of the aging temperature and also of the best annealing temperature of such alloys

Another matter of some concern in the study of irreversible transformations is the effect of cooling rate, particularly on Ar_3. The temperature at which that change starts is an important constant of any iron-base alloys In the particular alloy studied, Fig 4, Ar_3 starts at 273° C with a normal rate of cooling, but it might be expected to start at a slightly higher temperature if sufficient time were allowed Consequently, the specimen was again cooled from above Ac_3 and held for 21 hr. at a temperature below 300° C , most of that time close to 280° C. Nothing happened, which indicates that the temperature at which Ar_3 starts is not appreciably affected by rate of cooling in alloys of low carbon content

The opinion is rather widely held that the temperature at which Ar_3 starts is considerably influenced by the rate of cooling Undoubtedly that opinion is well founded, but it is based on the behavior of alloys containing carbon in excess of their limiting solid solubility In those alloys the amount of carbon retained in solid solution will vary with the rate of cooling and temperature from which the alloy is cooled Only carbon in solid solution has an influence on the temperature of Ar_3, but the effect of that carbon is very great. Hence in the presence of carbon or other elements affecting Ar_3 in quantities greater than their solid solubility limits, the temperature of Ar_3 will be affected by rate of cooling so far as it determines the amount of carbon remaining in solid solution. An extreme example is the Ar' and Ar'' transformations of high-carbon, low-alloy steels.

Although the start of Ar_3 is not appreciably affected by rate of cooling, the shape of the curve after the transformation begins is definitely modified by that factor. Thus on holding specimens for long intervals at temperatures below 273° C., the transformation continued to progress, but even in 18 hr. did not approach completion The displacement of the Ar_3 temperature from that corresponding to normal cooling was only 15° C. after that lapse of time. This phenomenon would be expected from the effects of self-induced pressure on the transformations, a subject discussed later.

OBSERVATIONS ON IRON-MANGANESE ALLOYS

The differential expansion curves of the low-carbon iron-manganese alloys are presented in the order of increasing manganese content, beginning with Fig. 5 In that figure only the A_3 transformations are observed. There are, however, indications of a slight discontinuity in the curves on heating at about 400° C. Other significant features are that Ac_3 is irregular, that Ar_3 does not go to completion at room tem-

peratuie and that more austenitc iemains in the alloy of highei manganese content

Going to somewhat highei manganese contents (Fig 6), the same phenomena aie observed, but the iieveisible expansion on heating is much more prominent   The Ar₃ tiansformation is carried further towards completion by taking the expansion curves down to the temperature of liquid air, but still it is not completed   Although the iieveisible expansion on heating interferes somewhat with estimation of the end point, it is evident that moie austenitc is ietained in the alloy of higher manganese content than in that of lowei content, not only at room temperature but at liquid-air temperature as well
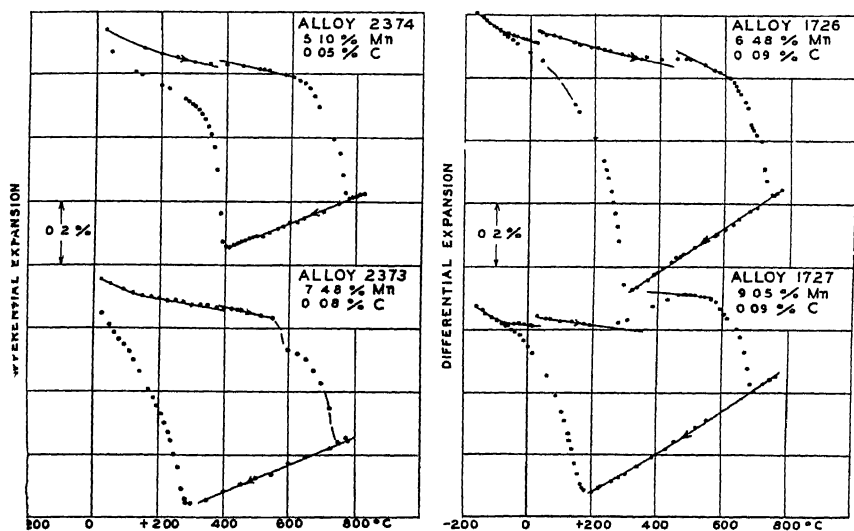
FIG 5 —DILATATION CURVES OF FE-MN ALLOYS CONTAINING 5 1 AND 7 5 PER CENT MN

FIG 6 —DILATATION CURVES OF FE-MN ALLOYS CONTAINING 6 5 AND 9 0 PER CENT MN.

The 9 per cent manganese alloy was again heated through Ac₃, top of Fig 7, but this time cooling was stopped at room temperature and the specimen reheated to 450° C   Again a prominent irreversible expansion was observed on heating between 300° and 400° C   These observations suggest that the irreversible transformation on heating is due to the further transformation of gamma to alpha iron, that is, to further progress of the change at Ar₃

Furthei information on the heating anomaly is furnished by the lower curve of Fig 7 taken on an 11 per cent manganese alloy   This alloy evidently contained more austenite than ferrite in its initial condition at room temperature   Three cycles of heating under Ac₃ and cooling in liquid air caused a large irreversible expansion which occurred

in small steps both on heating and on cooling   In the final heating cycle through Ac₃, the Ar₃ transformation went nearly to completion at liquid-air temperature   After the temperature cycles below Ac₃, the alloy was apparently completely in the alpha state, for a well-developed Ac₃ change was observed thereafter   These observations show definitely that the irreversible expansion on heating is caused by the transformation of gamma iron into alpha iron

With the next small increment in manganese content, 1 4 per cent, a new type of transformation appears (Fig 8)   To start with, this alloy
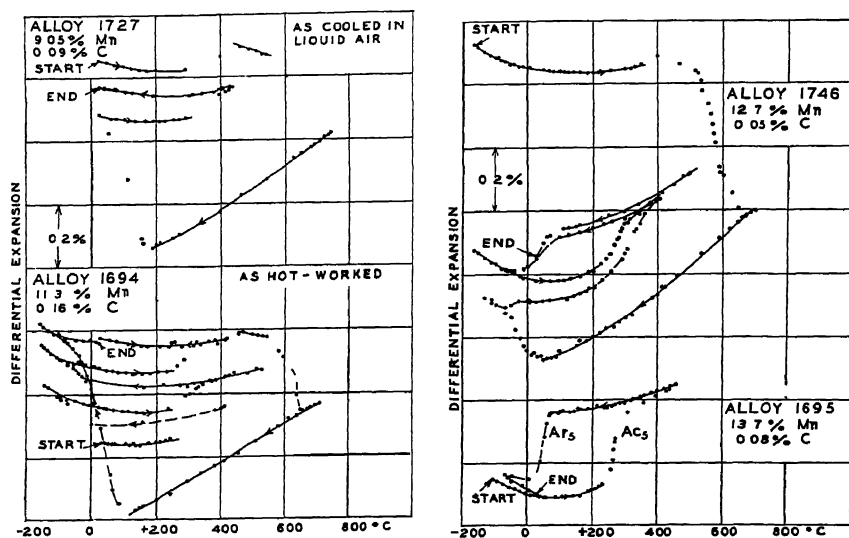
FIG 7 —DILATATION CURVES OF IRON-MANGANESE ALLOYS SHOWING EFFECTS OF CYCLIC HEATING BELOW Ac₃ ON INCOMPLETED TRANSFORMATION
FIG 8 —DILATATION CURVES SHOWING INTRUSION OF NEW IRREVERSIBLE TRANSFORMATION, THE VOLUME CHANGES AT WHICH ARE THE REVERSE OF THOSE AT A₃

was probably entirely in the alpha condition, as shown by the lack of an irreversible expansion on cooling in liquid air and on heating below Ac₃ Just how it was induced to assume that condition is unknown, but it is probable that cold working played a part   Thus, in an Fe-Ni-Co alloy, Ar₃ was found at a temperature about 30° C lower in the annealed condition than after cold working

When alloy 1746 is cooled from a temperature above Ac₃, Ar₃ starts at 50° C but does not progress very far even on cooling in liquid air Now on heating to above 400° C , but below Ac₃, a new transformation accompanied by a contraction on cooling was found and confirmed by a second temperature cycle   The reverse change, expansion on heating, occurs in nearly the same temperature range as the expansion attributed to the transformation of gamma to alpha iron   The closing of the loop

in the last heat cycle shows, however, that the gamma-alpha change is no longer involved

The new transformation identified by Ac₅ and Ar₅ is found alone in the 14 per cent manganese alloy of Fig 8 It is also found in three alloys of higher manganese content (Fig 9), but has diminished greatly in intensity at 20 per cent manganese (Fig 10) It disappears completely with manganese above 23 per cent in the presence of over 0 1 per cent carbon and a rather well defined inflection is found at about 115° C dividing a temperature range of low expansivity from one of high expansivity In the temperature range 50° to 200° C , the expansivity of the alloy increases from 12 to 20 millionths per degree Centigrade A reversible expansivity change of this type and degree has been observed previously only in the iron-nickel system

PRESSURE EFFECTS

The comparatively simple concepts of equilibrium between liquid and solid phases fail to provide an explanation for the complicated phenomena just described They neglect an important factor, namely, pressure, which when introduced appears to explain adequately phenomena associated with the gamma-alpha transformation

The mechanism of pressure development during the Ar₄ transformation has already been described [5] Briefly, when that transformation has advanced to a certain stage, a continuous network of alpha iron forms, completely surrounding the remaining austenite Further progress of the transformation causes pressure to develop in the austenite and attain a high magnitude The austenite units, of course, are microscopic in size The pressure builds up with progress of the transformation, consequently the temperature must be decreased further to cause the transformation to continue as required by the theorem of Le Chatelier Expansion curves observed during the progress of Ar₄ take just the course one would expect from the foregoing hypothesis, that is, the slope diminishes rapidly after the change is partly completed

In the converse case of a transformation occurring with a diminution of volume on cooling, such as Ar₅, three-dimensional tension will develop
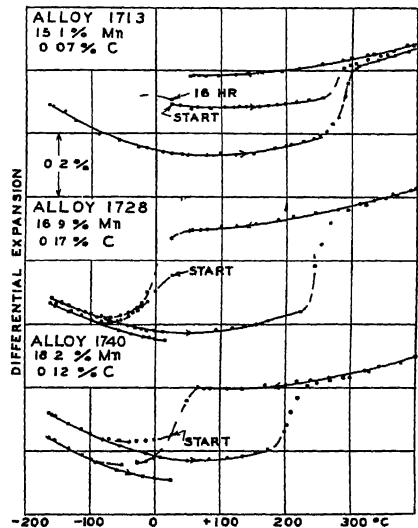
FIG 9 —DILATATION CURVES OF ALLOYS SHOWING NEW TRANSFORMATION

[5] H Scott Origin of Quenching Cracks U S Bur Stds Sci Paper 513 (1925)

but will act in the direction of restraining the transformation also The same is true of the transformations on heating, with the exception that, at the higher temperatures involved, the restraining network may have little strength and consequently be unable to sustain the high pressures necessary to produce an appreciable effect   In conformity with this proposition, the end of the Ac_3 transformation is sharp   The general principle may now be summarized as follows the temperature at which a transformation in the solid state involving a change in volume with change in temperature approaches completion is shifted in the direction of the imposed temperature change when the end product has sufficient strength to sustain high stresses

Examples of the conformity of the behavior of the A_3 transformations with this principle have already been given and the A_5 transformation offers others   In this case the temperatures of occurrence are so close that no appreciable difference in the shape of the curve on heating from that on cooling is found nor is to be expected   Going in either direction the completion of the transformation is appreciably retarded, but not to the degree that Ar_3 is retarded, because the volume change is much smaller

The principle of pressure restraint also serves to explain the expansion anomaly observed during the heating of alloys which display A_3 alone   The evidence presented here shows that this change is from austenite to ferrite, and this conclusion in regard to high-carbon steels is verified by X-ray studies [6] If, then, the retention of residual austenite at low temperatures is favored by pressure, it may be expected to transform to ferrite when heated to a temperature at which the restraining matrix softens materially, providing the tendency to transform still exists at that temperature   The assumption of the existence of a tendency to transform upon being heated to a temperature in the neighborhood of 300° C is not inconsistent with the onset of the gamma-alpha trans-

FIG 10 —DILATATION CURVES OF ALLOY IN WHICH NEW TRANSFORMATION IS DEPRESSED TO ROOM TEMPERATURE BY ALLOYING   OTHER CURVES SHOW DIS-APPEARANCE OF NEW TRANSFORMATION AT MANGANESE CONTENTS ABOVE 23 PER CENT AND REVERSIBLE CHANGE IN EXPAN-SIVITY WITH TEMPERATURE

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[6] K Heindlhofer and F L Wright Density and X-ray Spectrum of Hardened Ball Steel Tempered at Various Temperatures   *Trans* Amer Soc Steel Treat (1925) **7,** 34

formation at a much lower temperature on cooling, because nuclei of ferrite exist when this change is approached from below but not when approached from above

The temperature at which the ferrite network softens on heating is probably not greatly affected by composition in the high-manganese alloys concerned   Consequently, the irreversible transformation on heating would be expected to start at nearly the same temperature in the several alloys showing it   The end point of this change is evidently determined by proximity to Ac₃, and since Ac₃ is not lowered rapidly with increasing manganese content, the upper limit of the temperature range of the irreversible expansion should not change much with composition   These considerations account for the constancy of the temperature range of the irreversible expansion on heating

The permanent expansion on heating has not been observed in Fe-Ni alloys   That observation conforms also with the present view, inasmuch as the temperature of the Ac₃ transformation is much lower for a given temperature of Ar₃ in the Fe-Ni than in the Fe-Mn alloys   The temperature at which the ferrite softens, however, is probably not materially different in the former alloys from that in the latter   As a consequence the temperature range over which conditions are favorable for consummation of the gamma to alpha transformation on heating is much shorter in the Fe-Ni than in the Fe-Mn alloys, and evidence of that change has not been found in the Fe-Ni alloys   Thus the principle of pressure restraint accounts for a variety of phenomena associated with the transformations in iron-base alloys.

LOCATION OF AR₃

From the viewpoint of utility, perhaps the most valuable of the data given are those on the start of Ar₃ as a function of manganese content   To study this relation in more detail it is necessary to select characteristic temperatures from the several curves   The temperature of the start of Ar₃ given in Table 2 for each alloy was chosen because it is the most significant characteristic of that change, is easily recognized and is practically independent of rate of cooling   The temperature of the end of Ac₃ is also given because it is a critical temperature in heat treatment and is the only temperature that can be readily and accurately evaluated

Intensity values are also given in Table 2   They were obtained by taking the difference in expansion at the transformation temperature concerned between the reversible expansion curves of the metal before and after going through that transformation.   This operation requires an extrapolation for estimating the completion of Ac₃ which is uncertain in the cases left blank   Values for several Fe-Mn-Ni alloys are also given for comparison with the Fe-Mn alloys.

Precise location of the temperature of Ar_3 as a function of one component alone offers a rather complex problem because usually there is at least one other active element present in the alloy system studied   In the present case there are two, carbon and silicon, present in appreciable quantities   Furthermore, in our commercial alloys other active elements than those so far named usually are present   Hence if the composition

TABLE 2 —*Characteristics of Transformations in Fe-Ni-Mn and Fe-Mn Alloys*

Alloy No	Composition				End of Ac₃, Deg C	Start of Ar₃, Deg C	Intensity, Per Cent	
	Ni, Per Cent	Mn, Per Cent	C, Per Cent	Li, Per Cent			Ac₃	Ar₃
			IRON-NICKEL-MANGANESE ALLOYS					
1700	31 25	0 70	0 03	33 6	460	—80	0 16	0 40
1744	10 18	9 20	0 03	33 7		—80		
2375	5 02	5 11	0 045	18 6	710	280	0 43	0 64
2376	5 02	0 90	0 022	7 7	770	605	0 33	0 45
			IRON-MANGANESE ALLOYS					
2374		5 10	0 054	13 7	775	410	0 36	0 58
1726		6 48	0 09	17 8	740	305		0 75
2373		7 48	0 082	20 2	740	300	0 35	0 63
1727		9 05	0 09	24 2	690	190		0 54
1694		11 3	0 16	31 1	650	130		0 54
1746		12 7	0 05	32 6	660	50		0 91
					Start of Ac₅	Ar₅	Ac₅	Ar₅
1746		12 7	0 05		210	90	0 15	0 16
1695		13 7	0 075		240	70	0 25	0 27
1713		15 1	0 07		265	30	0 22	0 27
1728		16 93	0 17		230	40	0 30	0 32
1740		18 2	0 12		190	60	0 19	0 23
1739		19 8	0 11		160	25±	0 05	0 06
2469		19 06	0 22		155	25	0 31	0 37

transformation relation is to be generally useful, it must take into consideration the effects of the common alloying elements

The problem just stated was attacked in a previous paper[7] and the relative effects on Ar_3 of nickel, manganese and carbon evaluated in the presence of high contents of nickel   The data given here use the same relations and apply them to the problem of Fe-Ni-Mn-C alloy of high manganese content   In addition, the temperature range of applicability is greatly extended

[7] H Scott Expansion Properties of Low-expansion Fe-Ni-Co Alloys *Trans A I M E*, Inst of Metals Div (1930) 515

The system Fe-Ni provides the most convenient basis for undertaking the project mentioned, because it has been most thoroughly studied The literature provides two independent determinations of the relations between Ar₃ and nickel content [8] In both cases the alloys were so prepared that the content of other active elements was undoubtedly very low   Both sets of observations of the start of Ar₃ are plotted in Fig 11 and may be accepted as representative of pure Fe-Ni alloys   Very few points fall much off the curve of most probable location

Under the conditions of the previous work, manganese and carbon were found to be approximately 2 5 and 18 times as effective as nickel in lowering Ar₃   Comparison of the high-manganese with the high-
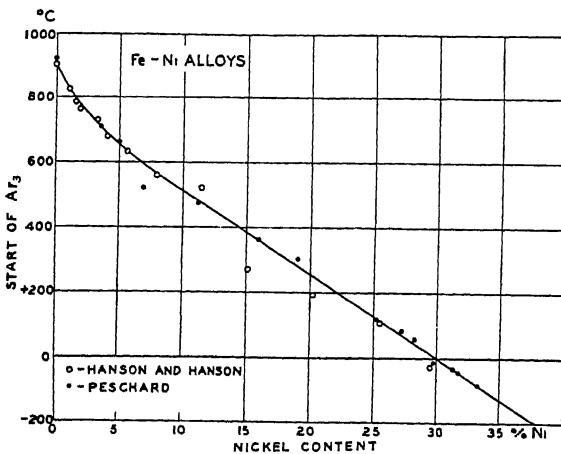
F$_{IG}$ 11 —T$_{EMPERATURE}$ OF START OF Ar₃ VERSUS NICKEL CONTENT OF PURE FE-NI ALLOYS

nickel alloys is consequently possible by expressing composition as equivalent nickel content, L, defined by

Per cent L = per cent Ni + 2 5 (per cent Mn) + 18 (per cent C) assuming that the constants of equivalence are accurate.   This relation ignores the undetermined effect of silicon content, which with a few exceptions is under 0 2 per cent and probably does not affect Ar₃ strongly Values of the equivalent nickel content are given in Table 2

Plotting the temperature at which Ar₃ starts in the several Fe-Ni-Mn and Fe-Mn alloys against equivalent nickel content yielded Fig 12 The curve for pure Fe-Ni alloys drawn as a solid line is taken from Fig 11 for the range of comparable compositions.   All of the values for

[8] D Hanson and H E Hanson   The Constitution of the Nickel-iron Alloys *Jnl* Iron and Steel Inst (1920) **102**, 39

M Peschard Contribution à l'étude des Ferro-nickels   *Rev de Mét* (1925) **22**, 581

Fe-Ni-Mn steels fall close to that curve, as do the values for Fe-Mn alloys having an Ar_3 point above 300° C   When Ar_3 in the Fe-Mn alloys starts below that temperature, the values fall at higher temperatures than given by the solid line and are represented by a broken line Consequently, one may conclude at once that the equivalence constant for manganese is accurate for Fe-Ni-Mn alloys containing 5 per cent nickel or more when Ar_3 starts between $+500$ and $-100°$ C

In the absence of nickel the equivalence constant of manganese holds for manganese contents under 7 per cent, but diminishes at higher contents   That is to say, a unit increase in manganese content is not so effective in lowering Ar_3 at contents above 7 per cent as below that value
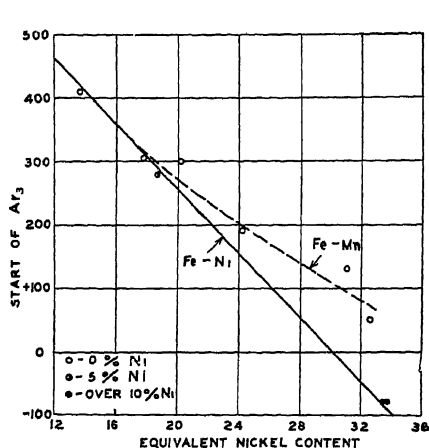
FIG 12 —RELATION OF START OF AR_3 TO EQUIVALENT NICKEL CONTENT IN FE-NI-MN-C ALLOYS
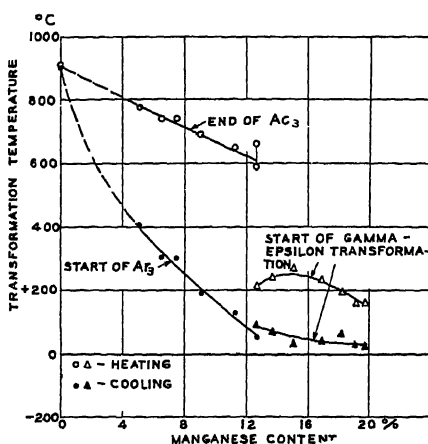
FIG 13 —TRANSFORMATIONS IN LOW-CARBON FE-MN ALLOYS PLOTTED AGAINST MANGANESE CONTENT

Otherwise the base curve for pure Fe-Ni alloys plotted against equivalent nickel content, as in Fig 12, gives with reasonable accuracy the start of Ar_3 in Fe-Ni-Mn alloys when the carbon is all in solid solution and the content of other active elements is low

As an illustration of the application of the foregoing relation, its use for determining the minimum alloy content of a nonmagnetic steel, usually an Fe-Ni-Mn-C alloy, may be mentioned   From Fig 12 an equivalent nickel content of 30 0 per cent depresses the start of Ar_3 to 0° C   Consequently, an alloy of that or higher equivalent nickel content will be nonmagnetic at room temperature provided the actual nickel content is not sufficiently high to bring the Curie point above room temperature

As a matter of fact, practical considerations usually demand that the start of Ar_3 be below $-100°$ C , otherwise the steel may become magnetic

on cold working or from moderate decarbonization   That requires an equivalent nickel content of 33 0 per cent   Hence we may define the minimum acceptable alloy content for a nonmagnetic steel by

Per cent Ni + 2 5 (per cent Mn) + 18 (per cent C) = 33 0

when the carbon content is below its minimum solid solubility limit and the content of other active elements is low

GAMMA-EPSILON TRANSFORMATION

The X-ray studies of Schmidt,[9] Ohman[10] and others have demonstrated the existence of a new phase, hexagonal close packed, called epsilon iron in iron-manganese alloys containing from 12 to 29 per cent manganese, more or less   This phase has a greater density than gamma iron so a transformation from the gamma to the epsilon phase should be accompanied by a decrease in volume   Just such a change is observed
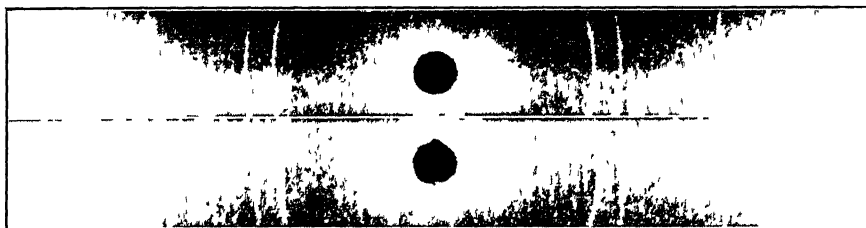
FIG 14 —X-RAY SPECTROGRAMS OF ALLOY 2469 (19 1 PER CENT MN, 0 22 C, 0 54 SI) TAKEN WITH DEBYE-SCHERRER CAMERA

a As annealed at 800° C   b After cooling in liquid air

here on cooling alloys containing between 12 and 23 per cent manganese Consequently, the transformation, identified by Ar_5 in Table 2, is probably that from gamma to epsilon and that identified by Ac_5 the change from epsilon to gamma

In an effort to verify this interpretation of the volume changes, E J. Haverstick of these Laboratories made X-ray spectrograms of alloy 2469 (Fig 10), both before and after cooling in liquid air   The length change of the test specimen produced by cooling in liquid air was measured and found to be 0 16 per cent, which corresponds closely with that of the expansion curve, so there can be no doubt as to the difference in constitution of the specimens tested   Nevertheless, no definite evidence of a change in content of the crystal species was found (Fig 14) In both spectrograms the lines of the gamma iron lattice are dominant, but both contain also relatively weak lines of the epsilon phase

[9] W Schmidt   Rontgenographische Untersuchungen uber das System Eisen-Mangan   Archiv f d Eisenhuttenwesen (1929) **3**, 293

[10] E Ohman   Rontgenographische Untersuchungen uber das System Eisen-Mangan   Ztsch f phys Chem (1930) **B8**, 81

The microstructure, on the other hand, shows pronounced evidence of a structural change. Fig. 15a is a photomicrograph of an initially polished but unetched surface of alloy 2469 after cooling in liquid air and Fig. 15b shows the same surface etched. The density of this sample changed from 7.918 before to 7.957 after cooling in liquid air, correspond-
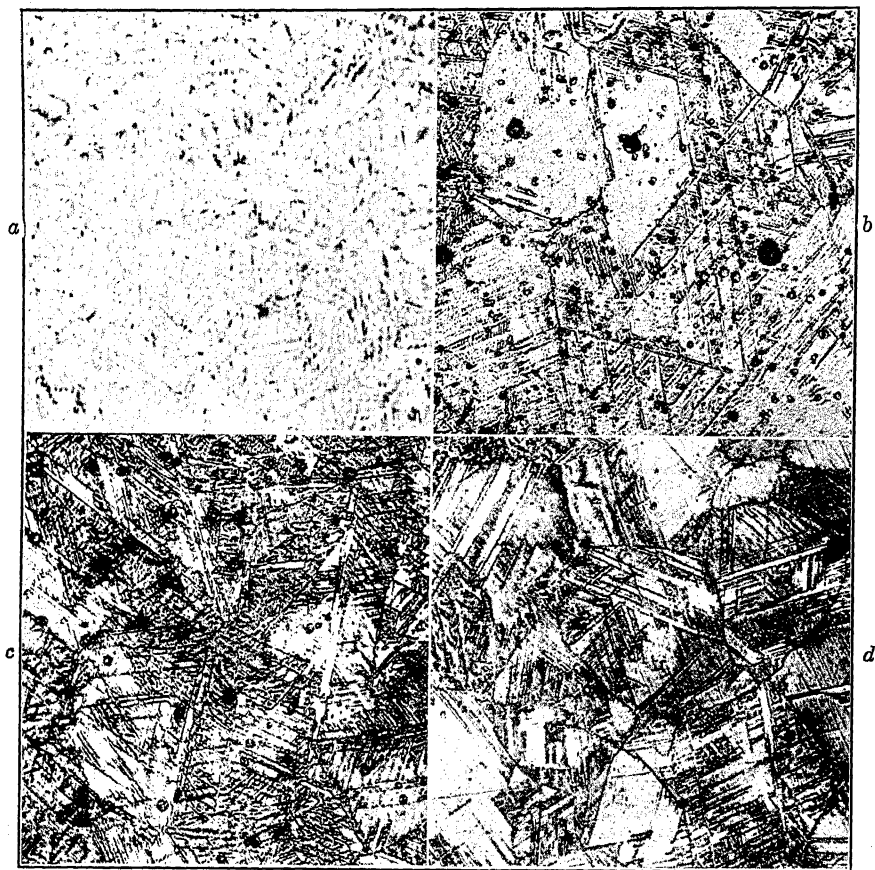
FIG. 15.—ALLOY 2469. COMPARE STRUCTURE OF SPECIMEN AS ANNEALED (c) WITH THAT OF SPECIMEN REPOLISHED AFTER COOLING IN LIQUID AIR (d).
Etching: 2 per cent nitric in absolute alcohol followed by swabbing with 1 per cent hydrochloric in absolute alcohol.
  a Polished surface after cooling in liquid air. × 100.
  b. Same as a but etched. × 500.
  c. As annealed. × 500.
  d. After cooling in liquid air. × 500.

ing to a volume change of 0.5 per cent, and the hardness increased from 209 to 272 V.P.N. That treatment produced a decided roughening of the surface, as was anticipated from the contraction observed (Fig. 10). The microstructure developed by repolishing and etching after cooling

in liquid air shows a marked increase in contrast between what appear to be two distinct constituents (Figs 15c and 15d)   The white constituent occupies more area and is more sharply defined after cooling in liquid air   It is surprising that so definite a structural change is not clearly revealed by the X-ray spectrograms

Some effects of manganese content on this transformation are shown in Fig 13   On heating it is found to begin between 150° and 250° C and on cooling between 100° and 25° C   Both the small separation between the changes on heating and that on cooling and the small effect of manganese content on its temperature are in sharp contrast with the corresponding characteristics of A_3 The chief effect of manganese is to cause the disappearance of this change when the manganese content exceeds about 23 per cent in the presence of 0 1 per cent carbon

There appears to be a moderate downward trend in the temperature of the gamma-epsilon transformation with increasing carbon or silicon content   This is indicated by the fact that alloy 2469, which is relatively high in these elements, is the only one in which the transformation is not well advanced after considerable time at room temperature   That phenomenon should be useful for further studies of the gamma-epsilon transformation by X-ray diffraction and metallographic methods

SUMMARY

Differential expansion curves taken on Fe-Mn alloys covering in small steps a wide range of compositions are presented   The curves are plotted so as to bring out clearly the irreversible transformations associated with phase changes

Several types of phase changes were recognized, as follows

1   The Ac_3 transformation or change from ferrite to austenite occurring with a decrease in volume during heating and the reverse change on cooling, Ar_3

2   A new transformation designated as A_5, which is accompanied by an increase in volume on heating (Ac_5) and a corresponding contraction on cooling (Ar_5)

3   An irreversible contraction on heating found only in a high-carbon alloy after rapid cooling from a high temperature

4   An irreversible expansion found only during the heating of alloys showing the Ar_3 transformation at a temperature which is nearly independent of the manganese content

Particular attention was paid to the location of Ar_3 because of its relation to the stability of austenitic alloys   The relationships between temperature of the start of Ar_3 and compositions of Fe-Ni-Mn-C alloys are expressed in a single curve in such a manner that the temperature of Ar_3 can be readily calculated from the composition for alloys differing widely in composition

Previous work indicates that the new transformation, Ar₅, is that from the gamma to the epsilon (face-centered cubic to hexagonal close-packed) phase X-ray spectrograms of an alloy for which the temperature range of this change was almost entirely below room temperature failed to show a strong epsilon line either before or after cooling in liquid air Decided changes in density and microstructure were observed after cooling comparison specimens in liquid air

The large permanent contraction found on heating a high-carbon austenitic alloy is shown to be caused by precipitation of carbide It is followed on heating above 550° C by a corresponding irreversible expansion associated with the re-solution of carbide This phenomenon provides a useful means for studying solid solubility and precipitation-hardening phenomena

The expansion anomaly on heating is shown to be caused by the transformation of residual austenite into ferrite To explain this and some of the other phenomena observed, the principle of pressure restraint is restated and applied The observed transformation characteristics conform very well to the requirements of this principle

ACKNOWLEDGMENTS

DISCUSSION

(Albert Sauveur presiding)

C WELLS, Pittsburgh, Pa (written discussion) —The difference in structure in Mr Scott's alloy containing 19 1 per cent manganese and 0 22 per cent carbon before and after liquid-air treatment is shown even more definitely at a magnification of 2100 A sample of this alloy supplied by Mr Scott was annealed in hydrogen, gently polished with magnesium oxide to remove the slight film left by the anneal, etched in 4 per cent nital, and photographed The structure shown is, of course, definitely polyhedral (Fig 16a) After being placed in liquid air the sample was again polished with magnesia and etched with nital (Fig 16b) The structure is that typical of our alloy containing 20 per cent manganese and 0 017 carbon

M A GROSSMANN, Canton, Ohio (written discussion) —Mr Scott has presented illuminating data on the behavior of iron-manganese alloys As he says, these are of particular importance because manganese is an inexpensive alloying element for steel Of particular interest is his detailed discussion of the gamma epsilon transformation which takes place at manganese contents between 12 and 20 per cent
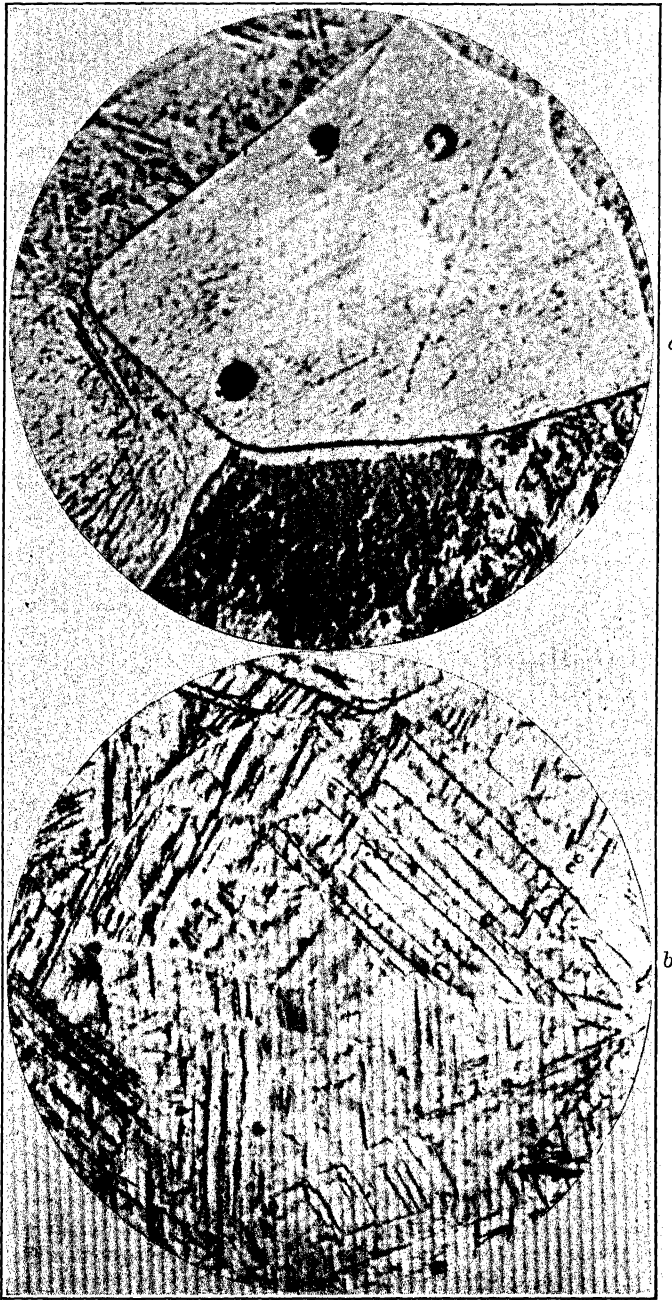
FIG. 16.—ALLOY 2469 (19.1 PER CENT MN, 0.22 PER CENT C, 0.54 PER CENT SI)
ANNEALED IN HYDROGEN, POLISHED WITH MAGNESIUM OXIDE AND ETCHED IN 4 PER
CENT NITAL. × 2100.
a. As annealed. b. After cooling in liquid air.

Certainly this must be borne in mind in any studies of the Hadfield manganese steels containing over 12 per cent manganese

In the discussion on page 288 regarding the effect on Ar₃ of the rate of cooling, a question arises as to what effect a very greatly retarded rate of cooling might have had at temperatures somewhat higher than those shown in Fig 4, for example, retarded cooling at 300° to 450° C instead of at 300° C It would be interesting to know whether Mr Scott has continued his experiments in this direction

Of further importance is his demonstration of how in this case also changes of volume may be used to distinguish between two different kinds of transformations

F H ALLISON, JR, Pittsburgh, Pa (written discussion) —It is safe to predict, owing to the increasing importance of austenitic corrosion-resisting and nonmagnetic steels, that the coming years will show great advances in our knowledge of gamma iron   Other methods of study than those which have proved most useful in the investigation of the ferritic alloys may assume a larger importance in revealing the characteristics of the gamma alloys   Mr Scott's able use of the dilatation method is an indication that a study of volume changes may yield valuable results

The author's equation expressing the relationship of manganese and carbon to nickel content is especially interesting   In general, it is confirmed by a number of alloys tested by the writer, both as to the effect of carbon and manganese, and although no attempt was made to check the exact evaluation of the constants, the alloys grouped themselves remarkably well within the limits set by the equation

There are some theoretical considerations which indicate that the manganese equivalent should be slightly lower than 2 5   Thus, if the Ar₃ curves for nickel and manganese shown in Figs 11 and 13 respectively be extrapolated to absolute zero, the transformation disappears entirely at about 41 per cent nickel or 20 per cent manganese   With allowance due to impurities and experimental error, these values are significantly close to 38 7 per cent nickel and 18 5 per cent manganese, percentages that correspond respectively to six and three corner atoms in the unit cube of alpha iron   This ratio of nickel to manganese gives the value of 2 09   The actual ratio of equivalence calculated from the author's data shows an approach to this value with manganese contents above 6 5 per cent   At lower percentages, the large initial effect of manganese additions, as shown by the slope of the curve below 6 per cent manganese in Fig 13 of the paper, seems to increase the effectiveness of manganese considerably above the theoretical amount

C L SHAPIRO, Cambridge, Mass (written discussion) —An investigation was started last February at Harvard University, under the supervision of Professor Sauveur, concerning the solubility of metals with each other and the formation of solid solutions and intermetallic compounds   As a basis for this investigation, the different metallic binary systems were collected and reviewed, in all, 350 different systems were compiled, with many variations, totaling 500   This collection could have easily been extended to 1500 or more

This convention has contributed eight new modifications of binary diagrams, the Institute of Metals in England held a meeting last week and presented seven, conferences in France, Germany, Japan and Sweden will bring the total up to a very small figure of 25 for each semi-annual convention   Thus 50 are presented yearly at conferences and approximately 50 are published in periodicals, bringing the sum to 100 yearly   The confusion existing today will be nothing compared with that within a period of 10 years, in which there will be a thousand new modifications on approximately 50 systems   With the universal use of the X-ray this amount will be passed easily   It will be nearly as bad as the patent problem of today, but not as serious, since patent rights cannot be torn up or disregarded as easily as a society's bulletin   An illustration of this confusion is the iron-manganese and copper-silver systems.

There were four different papers presented within the past year on the non-manganese system by four different authors with four different diagrams   Today's paper is a variation from the rest   There were seven copper-silver modifications in the past year and one was presented last week in England and this society had one read last Tuesday morning, totaling nine in one year

What is the reason for all this confusion?   The purity of the metal used, the human element or the method of determining the solubility, liquidus and solidus?   All authors claim that the purity of their metal is as nearly perfect as possible   So, being true scientists, we cannot consider the purity of the metal as the cause of the variation   The human element also can be disregarded, as metallurgists are nearly perfect   Finally, the method of determining the liquidus and solidus   The first equilibrium diagram was formed by slow cooling, then slow cooling and annealing for a short period of time   This year in France Mr Bronieksli and Strasburger annealed their copper-zinc alloys up to 50 atomic per cent for 1000 hr and over 50 atomic per cent 3000 hr @ 400° C , which is the marathon annealing record   Their results vary with the rest

In 1927, there were 27 continuous series of solid solution diagrams   Today we have only 11 left, 16 were found to form intermetallic compounds or solid solutions by annealing at high temperature for long periods of time   Within a few years there will be no maximum or minimum equilibrium diagrams   Two of the remaining 11 are on the doubtful list and will have their compounds identified shortly

The rate of cooling varies with each diagram, the universal practice in cooling from the annealing temperature is to shut off the supply of heat and cool the sample in the furnace   Another method, which is little used, is the gradual lowering of the temperature by intervals, thus reaching atmospheric temperature slowly   Comparing these two methods, the first is a mild form of quenching, while the second is true annealing

Will the solubility of the metal remain the same if annealed at a longer period of time?   A question was asked in the discussion following Mr Ziegler's paper in the A S S T meeting this week "Was there any difference in the sample when kept ½ hr , 1 hr and 2 hr in the atmosphere of oxygen?"   His reply was in the negative   Will there be a difference after 3000 hr of heating, due to coagulation of the minute particles in or out of solid solution, which is facilitated by the long annealing time and temperature?

The temperature of annealing usually is near or just below the eutectic temperature   Referring to the silver-copper, the annealing temperature began at 400° C for 408 hr , decreasing to 24 hr at 775° C   The eutectic temperature is 779 4° C

The recrystallization temperature of copper and silver is 200° C respectively and if added together the recrystallization temperature will be 400° C   Usually the temperature is lower than the sum of the two   By long annealing, the higher the temperature above that of recrystallization, the greater will be the variation

YAP, CHU-PHAY, New York, N Y —What is the advantage of plotting differential expansion in that way?   It seems to me there is no very sound mathematical justification for it   Do you know why?

F M WALTERS, Pittsburgh, Pa —Personal preference

YAP, CHU-PHAY —I believe there are other methods which probably will show the critical point much better

I am what you might call a great believer in the use of the phase rule   I always like to see how the phase rule works out in metallic systems

For example, we draw a diagram showing the irreversible Ar₃ and Ac₃ transformations   I have not read the paper carefully, but Dr Walters mentioned that the transformation is not completed   I imply from that statement that he assumes

there will be only one single phase at any temperature   I think we all know that in the binary system, in going from one phase to another we always have an intermediate heterogeneous field

I was much interested in the discussion of Mr Shapiro because I have an ax to grind and it fits in very well with some of my ideas of the future methods of studying the diagrams   We have studied the silver-copper system and spent years and years studying the variation in the solubility curve   For example, several times in the past, as I have pointed out, the solubility curve will be affected by the particle size of the solute in contact with the solid solution

Perhaps in the future, too, we will not waste so much time in making an anneal of 300 hr or 1000 hr to get equilibrium   We will probably study by means of constructing a diagram of this sort from studies on electrode potentials   A part of the diagram will show free energy, a part composition, and a part temperature   By taking segments at constant temperature, you could construct a whole diagram on the basis of such figures

Such diagrams will be equilibrium diagrams and not the diagrams we have today which we call equilibrium diagrams   I think we have abused the term "equilibrium diagrams"

F M WALTERS —I will attempt to answer only two or three questions which have been raised in the discussion from perhaps more my own experience than anything that is given in Mr Scott's paper

If we take 7 per cent iron-manganese alloy with relatively low carbon, the beginning of the transformation range, gamma to alpha, is at approximately 350° C   We have held at 630° C 17 hr without getting any transformation   At 400° C we have held 42 hr without getting any transformation   Of course, that is not long enough   We will build apparatus to find out what happens in three months, possibly

In regard to Mr Yap's remarks about the degree of completion of the transformation, we have in the alpha solid solution one rather definite coefficient of expansion which differs greatly from the coefficient of expansion of the gamma solid solution   If we draw a diagram of the transformations of the alloys from zero to 7 or 8 per cent Mn, so that the expansion curves for gamma iron coincide, the expansion curves for alpha iron fall within an envelope extrapolated from low-manganese content alloys, which defines the limit of the expansion at Ar_3 The transformations to first approximation occur between those lines, so when the expansion at Ar_3 fails to reach the alpha envelope, we are confident that the transformation has not been completed   Failure of the transformation, gamma to alpha, to go to completion depends upon the rate of cooling and on pressure phenomena

M GENSAMER, Pittsburgh, Pa (written discussion) —Mr Scott has pointed out that his X-ray crystallographic studies did not substantiate the idea that the new transformation encountered was the change from the gamma to the epsilon phase, recently studied by a number of investigators   He kindly gave us a piece of his alloy containing 19 1 per cent manganese and 0 22 per cent carbon, in which the contraction on cooling began at room temperature, while the expansion on heating did not begin until 150° C , so that a specimen cooled to room temperature from 500° C should be nearly completely in the gamma condition, but could be made to transform by further cooling   This alloy should be a convenient one for studies such as an X-ray crystallographic one   Our results on this alloy show definitely that the gamma to epsilon transformation is the one that takes place   The transformation is not complete, which is in accord with Mr Scott's dilatometric studies, since he shows a length change of about 0 16 per cent. whereas the complete transformation would require about 0 6 per cent change in length. as calculated from the lattice dimensions of the two phases in a similar alloy

It has been found that unless considerable care is taken in the preparation of the specimen for examination before immersion in liquid air, epsilon lines appear which are entirely absent in a cautiously prepared specimen, this probably accounts for the negative results obtained by Mr Scott's associate   It was found necessary to etch the specimen deeply after immersion in liquid air, since otherwise no epsilon lines were obtained   For some reason the gamma phase near the surface does not transform to the epsilon phase when the temperature is lowered   Mr Scott's pressure considerations may account for this stability of the gamma phase near the surface

H Scott (written discussion) —Before responding to the written discussion of this paper I wish to thank Dr Walters formally for presenting it, for replying to discussion from the floor, and for his illuminating comments on the work   His replies to the oral discussion are adequate and entirely in accord with my views, so that matter requires no further mention

Mr Wells' photomicrographs of alloy 2469 taken at a very high magnification before and after cooling in liquid air are a distinctive contribution to the subject They show, as does Fig 15, a well defined change in the structure of this alloy during the gamma to epsilon transformation   The structure found by him, however, is somewhat different from that given in the paper   For a check, the experiment was repeated by Miss Ferguson, at our Research Laboratories, who took the first photomicrograph (Fig 17) immediately after annealing in order to avoid so far as possible any progress of the transformation at room temperature   The same area was photographed after cooling in liquid air and repolishing the roughened surface, starting with a coarse wheel   The change in structure is now much more clearly defined and corresponds better with the photomicrographs shown by Mr Wells   The remaining differences should be attributed to the different polishing technique and magnification

We are indebted to Mr Gensamer for a positive identification of the crystal structure of the same alloy before and after cooling in liquid air, and for an explanation of our previous inability to get consistent results from the X-ray diffraction patterns His findings remove any doubt as to the nature of the discontinuous contraction on cooling identified by Ar_5 in the paper   The observations of Messrs Gensamer and Wells constitute a valuable experimental contribution to the paper

Mr Grossmann properly suggests that the gamma-epsilon transformation should be considered in studying the Hadfield manganese steel   It is doubtful, however, whether this transformation can be developed in that alloy, because a high carbon content tends to suppress it when the carbon is in solid solution   His second point is covered by Dr Walters' reply to Mr Yap's discussion, but it is well to emphasize the fact that the constancy of Ar_3 with changing cooling rate is contingent on the carbon content being less than its minimum solid solubility in gamma iron

Mr Grossmann's question on the identification of the transformations revealed by expansion anomalies is pertinent because it is a thing that the operator is likely to take for granted   There are six distinctive characteristics of the expansion anomalies which contribute to their identification (1) temperature of the change, (2) direction of the change, that is, expansion or contraction, (3) intensity, (4) shape of the curve, (5) whether or not a related change occurs both on heating and on cooling, and (6) continuity of the transformation throughout a series of alloys starting from a simple and familiar one   Having six characteristics and only three established kinds of transformations in the Fe-Mn-C system, there have arisen few if any cases in which the identity of a change is debatable   If the criteria just noted prove inadequate, microscopic examination, magnetic tests and X-ray diffraction analysis are in reserve to apply to debatable cases

It is gratifying to learn from Mr Allison that the writer's general expression for the temperature of Ar_3 in terms of nickel, manganese and carbon contents has been confirmed   He suggests an ingenious means for arriving at a theoretical value of the

ratio of equivalence between nickel and manganese in lowering Ar_3. That method rests, however, on a demonstration that the temperature of Ar_3 must necessarily fall to absolute zero at certain integral ratios of manganese and nickel to iron atoms. This novel concept is worthy of analysis from the viewpoint of atomic theory.

The writer is unable to concur with Mr. Shapiro in his pessimistic opinions concerning the future consequences of the number of new constitutional diagrams appearing in the literature.   On the other hand, the prospect appears gratifying, for in the
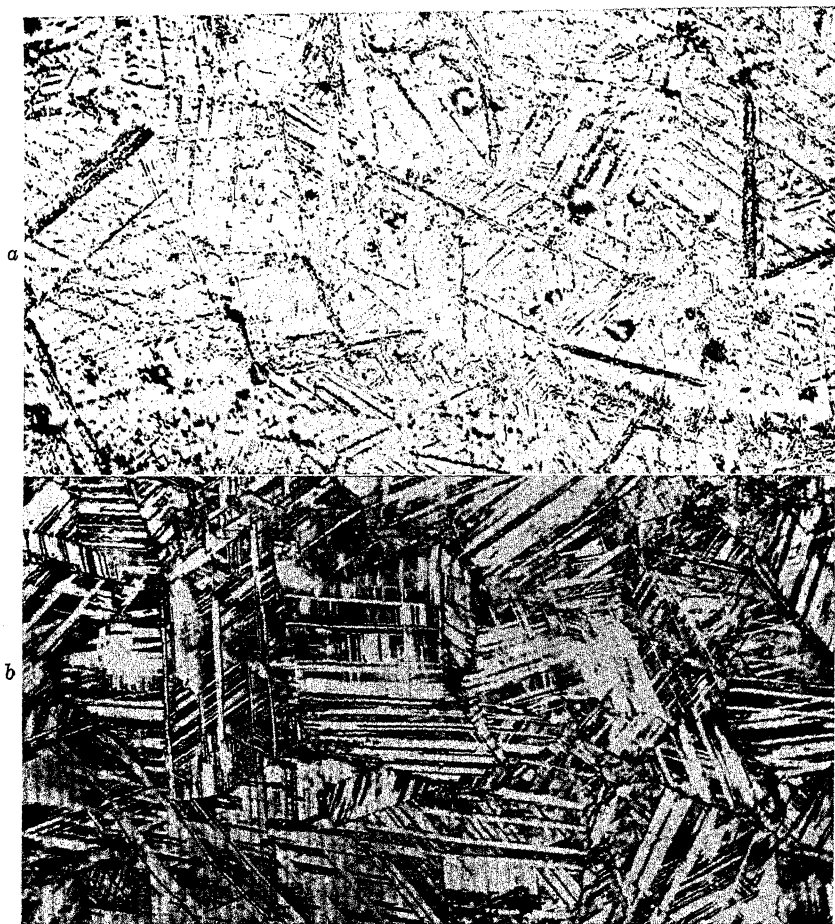
FIG. 17.—SAME ALLOY AS FIG. 16.   × 500.   a. AS ANNEALED.   b. COOLED IN LIQUID AIR, POLISHED AND ETCHED.

past increased work in a particular field has consistently tended to dispel confusion, although frequently increased complexity is the price paid. The abandonment of some simple notions incompatible with later findings is an evidence of healthy scientific development.   Only when details are intimately known and understood does it become possible to formulate trustworthy generalities that again bring simplicity.   His remarks on times required to reach equilibrium are directed evidently towards other papers on the program, for no suggestion was made here of an effort to establish an equilibrium diagram for the Fe-Mn system.

Composition Limits of the Alpha-gamma Loop in the Iron-tungsten System

By W. P. Sykes,* Cleveland, Ohio

IN an earlier paper[1] the composition-temperature limits of the gamma iron phase in the iron-tungsten system were reported as approximated
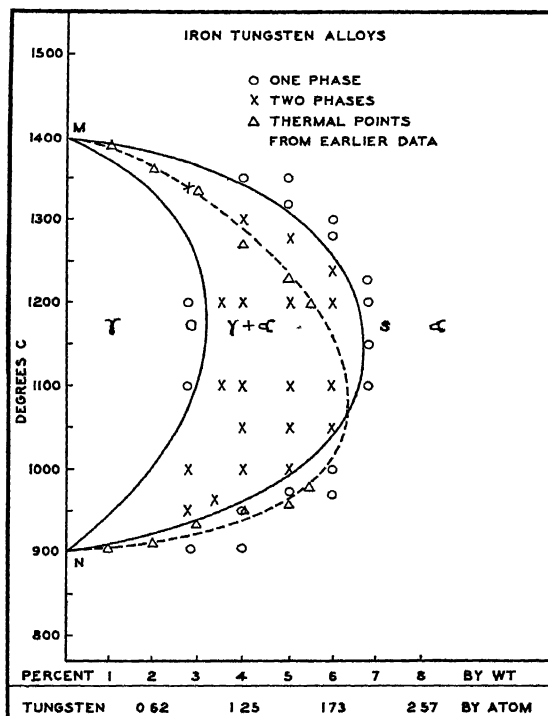
FIG 1 —DIAGRAM OF ALPHA-GAMMA LOOP AS DETERMINED BY MICROSTRUCTURE AND THERMAL ANALYSIS

by thermal analyses   At that time no attempt was made to develop metallographic evidence of the coexistence of two phases in the iron-rich solid solution at temperatures between 900° C and 1400° C

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* Metallurgical Engineer, Cleveland Wire Works, General Electric Co
[1] W P Sykes The Iron-tungsten System   Trans A I M E (1926) 73, 968

The temperature-phase relations of the solid solutions of tungsten in gamma and in alpha iron as determined by a microstudy of a series of heat-treated specimens are shown in Fig 1   The alloys used for this investigation were prepared by melting the briquetted metal powders in a hydrogen atmosphere at 1550° to 1600° C in alundum boats   After having been held at this temperature range for about 1 hr the melts were cooled slowly through the freezing range to about 1450° C, held for 2 hr at this temperature and quenched in water

In compositions below about 3 per cent tungsten, such a quench from the delta range results in a fragmented structure, characterized by the serrated grain boundaries seen in Fig 2   By reheating such a specimen for a few hours at 800° to 850° C this microstructure is strikingly altered to one marked by the large polygonal grains shown in Fig 3   As might be expected, this increase in grain size is accompanied by an appreciable softening of the material

With increase in tungsten content, this fragmented structure of the quenched alloy is gradually replaced by one of larger grains, more regular in outline, until at about 5 per cent tungsten the alloy as quenched from above 1350° C exhibits a structure similar to that shown in Fig 3   This type of grain persists up to about 30 per cent tungsten and represents the solid solution of tungsten in body-centered iron, as has been shown from diffraction patterns [2]

If, however, an alloy of tungsten content between approximately 3 and 6 per cent be slowly cooled from 1400° C to about 1200° C, held at the latter temperature for several hours and quenched, the outlines of a second phase appear in the microstructure (Fig 4)   The detection of two phases in the microstructure within this range of composition and temperature has been noted by Arnfelt [3]   The well-defined boundaries after such a quench rapidly fade upon reheating to about 900° C for a short time, as can be seen in Fig 5   After heating for 2 hr at 900° C, the alloy again appears to consist of the large grains of a single phase

While the microstructure might seem to indicate the presence of two phases in such alloys as quenched from the gamma range, the X-ray diffraction patterns show only the lines of the body-centered lattice This fact has been mentioned by Arnfelt and confirmed at the Cleveland Wire Works laboratory   It appears, then, that gamma iron, dissolving at most some 3 per cent of tungsten at about 1200° C, changes to the alpha modification even when cooled by a drastic quench   After quenching, the boundary lines seen in the microstructure enclose areas of fine-grained body-centered iron unsaturated with tungsten at room tem-

[2] E P Chartkoff and W P Sykes X-ray Notes on the Iron-molybdenum and Iron-tungsten Systems   *Trans A I M E*, Inst Met Div (1930) 566

[3] H Arnfelt On the Constitution of the Iron-Tungsten and Iron-Molybdenum Alloys   *Carnegie Schol Mem*, Iron and Steel Inst (1928) **17**, 1

perature. Subsequent heating at temperatures slightly below 900° C. allows the tungsten content to be equalized by diffusion, at the same time resulting in growth of the small grains or their absorption by the large alpha grains present in the quenched state. At higher magnifications
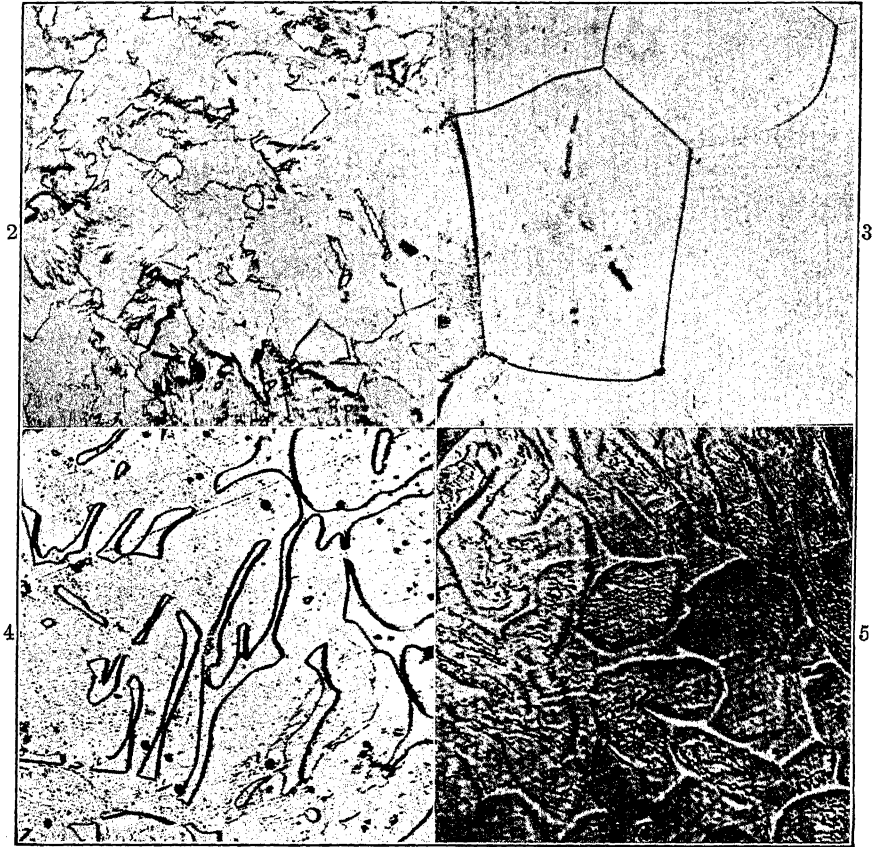
FIG. 2.—FE + 2.8 PER CENT. W. QUENCHED FROM 1450° C. AFTER SOLIDIFYING FROM MELT. × 200.

FIG. 3.—FE + 2.8 PER CENT. W. REHEATED FOR 5 HR. AT 850° C. AFTER QUENCHING FROM 1450° C. × 200.

FIG. 4.—FE + 4.7 PER CENT. W. AFTER FREEZING, COOLED FROM 1350° TO 1200° C. IN 1 HR.; HELD 2 HR. AND QUENCHED. × 200.

FIG. 5.—FE + 4.7 PER CENT. W. HEATED 2 HR. AT 1200° C. AND QUENCHED. REHEATED AT 900° C. 5 MIN. AND QUENCHED. × 200.

the areas presumably occupied by the face-centered phase at 1200° C. are suggestive of a fine-grained material (Fig. 6).

Alloys containing up to 6 per cent. tungsten are always considerably harder as quenched from the gamma range than after subsequent heatings at 900° C. This effect is dependent upon a sufficient time at both

temperatures to approximate equilibrium. For example, the 3 per cent. tungsten alloy as quenched from 1200° C. shows a Rockwell B hardness of 80. Its microstructure is of the type shown in Fig. 2. After heating at 875° to 900° C. for 5 hr. the hardness is reduced to B-60, and the structure is that illustrated by Fig. 3.
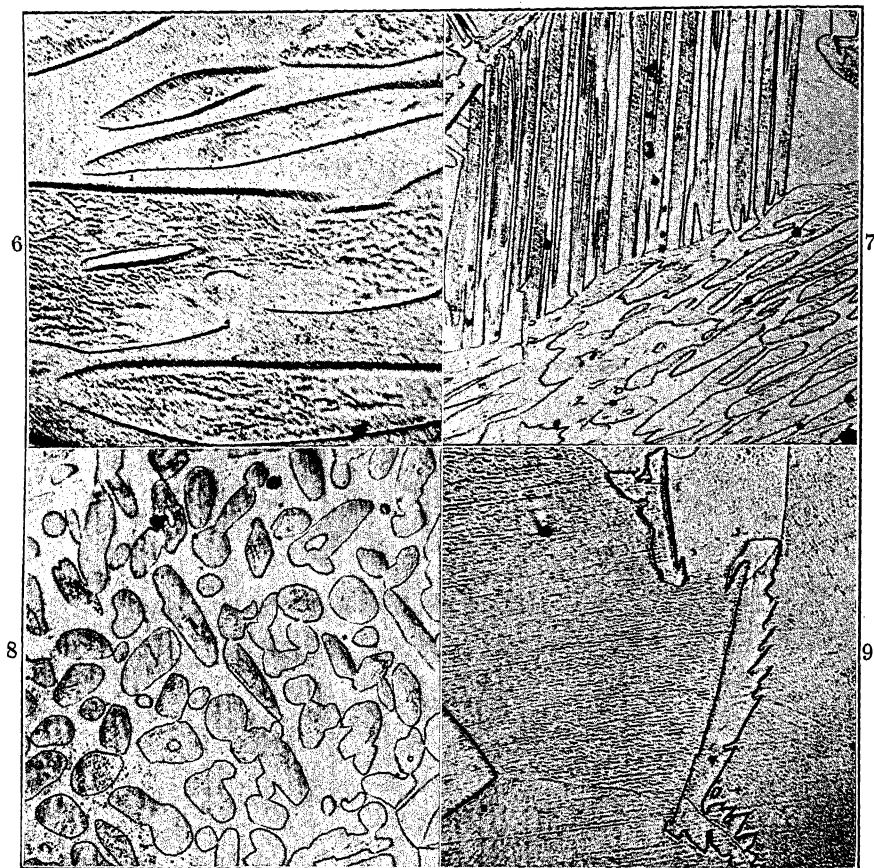
FIG. 6.—FE + 5 PER CENT. W. COOLED FROM 1450° TO 1200° C. IN 1 HR.; HELD AT 1200° C. FOR 3 HR. QUENCHED. × 500.
FIG. 7.—FE + 5 PER CENT. W. SAME SPECIMEN AS IN FIG. 20. × 100.
FIG. 8.—FE + 5 PER CENT. W. QUENCHED FROM 1450° C. REHEATED AT 1200° C. FOR 3 HR. QUENCHED. × 100.
FIG. 9.—FE + 5.1 PER CENT. W. QUENCHED FROM 1450° C. REHEATED AT 850° TO 900° C. 5 HR. THEN AT 1000 ± 10° C. FOR 30 MIN. AND QUENCHED. × 200.

The gamma phase may assume two characteristic shapes, which seem to be determined by the conditions of heating or cooling under which it is formed. Slow cooling into the region of two phases develops groups of slender parallel bands, sometimes accompanied by lens-shaped areas, as shown in Fig. 7. If the alloy made up of the coarse-grained body-

centered phase be placed in the furnace at, say, 1200° C and held for 1 hr the gamma phase develops in circular areas, as if the transformation had started from centers rather uniformly distributed (Fig 8)   A similar occurrence has been described by Grossmann[4] in his studies of the iron-chromium alloys

In compositions lying between 3 and 6 per cent tungsten, the upper limit of the two-phase range can thus be determined by slow cooling to a series of decreasing temperatures, holding at such temperatures for several hours and quenching   At 1100° C and above, equilibrium appears to be approached after 3 hr , since longer heating results in no further change in relative quantities of the two phases   In locating the tungsten-rich boundary of the two-phase region (from N to S, Fig 1) the alloys subsequent to quenching from 1450° were heated for 10 hr   at 800° to 850° C   This treatment resulted in the coarse microstructure shown in Fig 3, representing the solid solution of tungsten in alpha iron

With such an initial microstructure the first formation of the gamma phase is readily detected upon heating to temperatures above 900° C and quenching   In Fig 9 is shown a small area marking the formation of the gamma phase at the grain boundary of the alpha solid solution This 5 1 per cent tungsten alloy, after heating at 850° to 900° C for 5 hr was then heated at 1000° C $\pm$ 10° C for an additional 30 minutes

In compositions below 2 5 per cent tungsten, grain growth in the alpha phase formed during the quench takes place very rapidly and in the resulting fragmentary structure it is difficult to distinguish the areas formerly occupied by the gamma phase

The temperatures of phase change, as previously determined by the thermal point study and indicated by the dashed curve in Fig 1, agree fairly well with the ranges as determined by observation of microstructures

DISCUSSION

(Albert Sauveur presiding)

M A Grossmann, Canton, Ohio (written discussion) — With his usual accuracy, Mr Sykes has added another clarifying chapter to his many fundamental studies of the iron-tungsten system   As stated by the author, these duplex structures have indeed been observed in this and other alloys in the presence of carbon, and isolated instances have been observed elsewhere   But so far as we are aware, this is the first time that a systematic study of such structures has appeared for a binary system only

It may be of interest to state that structures similar to those of the author's Figs 4 and 5 can be observed in low-carbon steels containing between 0 4 and 0 8 per cent tin   As pointed out by Wever, approximately 2 per cent tin suppresses the alpha-gamma transformation   In the case of the above mentioned steel, containing

[4] M A Grossmann   Nature of the Chromium-iron-carbon Diagram   *Trans* A I M E (1927) **75,** 214

say 0 6 per cent tin, when quenched from about 1550° F it will exhibit a structure quite similar to Mr Sykes' Fig 5 If quenched from about 1725° F the structure will be similar to that of Mr Sykes' Fig 4 These would therefore be in a range of duplex structures analogous to those shown by Mr Sykes in iron-tungsten alloys

YAP, CHU-PHAY, New York, N Y —I cannot let this occasion pass without paying my compliments to Mr Sykes for a beautiful piece of work Mr Sykes, independently of the German metallurgists, was the first to call attention to the closed gamma loop I think I am correct in that, although Mr Bain showed a similar diagram for Fe-Cr alloys at about the same time It required courage to propose the closed gamma loop at that time, when we had had no examples of it in other systems

I have been interested in Fig 8, which is characteristic of what is called an emulsoid in colloidal chemistry You have two solutions, alpha and gamma, which would correspond to water and ether, or oil and water Then if you add some kind of emulsifying agent or a third solute, and shake it up, you can get an emulsoid in which the fine particles of oil will be dispersed in the water

I should like to ask Mr Sykes' opinion on the interpretation of Fig 8, because I think it has much more significance than we can see at present

E C BAIN, Kearny, N J —It is particularly interesting to note that the iron-chromium system and the iron-tungsten system have marked similarity not only in the fact that they both show this loop wherein the austenite or face dominated by gamma iron is the stable one, but that the limit of solubility for chromium and for tungsten appears to be about one atom in eight in the gamma iron That probably applies also to molybdenum, and does not apply quite definitely to silicon, tin, vanadium, and some others which have a very much lower solubility

W P SYKES —In connection with the type of structure shown in Fig 8, I can only say that this is typical of the structure developed when the solid solution, we will say the body-centered cubic solid solution, is heated from below the range into the range of the two-phase field

That is to say, the transformation seems to start from centers and grows outward, forming more or less rounded areas of the second phase (second solid solution), whereas if you cool from above into this range the second phase develops with more or less directional properties I am sorry I am unable to give you any deeper interpretation of that picture

Magnetic Properties Versus Allotropic Transformations of Iron Alloys

By T D Yensen[*] and N A Ziegler,[*] East Pittsburgh, Pa

(Boston Meeting, September, 1931)

Effect of Elements on Magnetic Properties of Iron

The elements aluminum,[1] arsenic,[2] silicon,[3] tin[2] and vanadium,[4,8] when used in relatively small amounts as alloying elements, seem to have a beneficial effect on the magnetic properties of iron—i e , they increase the maximum permeability and decrease the coercive force—whereas there are definite indications that boron,[5] carbon,[6] nitrogen,[7] oxygen,[8] phosphorus,[6] sulfur[6] and titanium,[4] as well as the metals of and adjacent to the ferromagnetic group, nickel,[9] cobalt,[10] copper,[11] and manganese,[6] have a detrimental effect on these properties

The effects of calcium[4] and magnesium[4] are small, if any, while the effect of chromium[12] in small amounts is unknown and in large amounts is generally detrimental

Wever's Classification[13]

All chemical elements may be divided into three classes based on their effect on the allotropic transformation points of iron   Class 1 contains the nonmetallic elements (except phosphorus) and these lower the A_3 point and raise the A_4 point   Class 2 contains the common metals and

* Research Laboratories, Westinghouse Elec & Mfg Co
[1] T D Yensen and W A Gatward Univ of Illinois Eng Expt Sta Bull 95 (1917)
[2] C F Burgess and J Aston Electrochem & Met Ind (1909) 7, 403
[3] T D Yensen Univ of Illinois Eng Expt Sta Bull 83 (1915)
[4] T D Yensen Unpublished
[5] T D Yensen Univ of Illinois Eng Expt Sta Bull 77 (1915)
[6] T D Yensen Trans Amer Inst Elec Engrs (1924) 43, 145
[7] W Koster Archiv f d Eisenhuttenwesen (1929–1930) 3, 637
    E Lehrer Ztsch f Elektrochemie u angew Physik (1930) 36, 460
[8] N A Ziegler Unpublished
[9] T D Yensen Trans Amer Inst Elec Engrs (1920) 39, 791
[10] G W Elmen Bell System Tech Jnl (1929) 8, 435
[11] C F Burgess and J Aston Met & Chem Eng (1910) 8, 79
[12] F K Fischer Rensselaer Poly Inst Bull , Eng and Sci Series, 28 (1930) 49, 839
[13] F Wever Stahl u Eisen (1929), Archiv f d Eisenhuttenwesen (1929) 2, 739

phosphorus, and these raise the A_3 point and lower the A_4 point until, for a certain composition, the A_3 and A_4 points coincide, resulting in the so-called closed gamma loop   Class 3 contains the elements that, as far as we know, are insoluble in iron, namely, the alkalies and the alkaline earth elements

In this classification the elements of and adjacent to the ferromagnetic group—nickel, cobalt, copper and manganese— as well as zinc and some of the rare metals and the elements of the platinum group belong in class 1

EFFECT OF ELEMENTS ON MAGNETIC PROPERTIES FOLLOWING WEVER'S CLASSIFICATION

In Table 1 the elements are arranged according to Wever's classification, and their qualitative effect on the magnetic properties of iron have been indicated   This shows that all the elements of class 1 (i e, those that lower the A_3 and raise the A_4 points) have a bad effect[14] on the magnetic

TABLE 1.—*Wever's Classification of the Elements and Their Effect on Magnetic Properties of Iron*

Class 1 Element Decreases A_3			Class 2 Element Increases A_3			Class 3 Element Insoluble in Iron		
Element	Type of Space Lattice	Effect on Magnetic Properties of Iron	Element	Type of Space Lattice	Effect on Magnetic Properties of Iron	Element	Type of Space Lattice	Effect on Magnetic Properties of Iron
B	?	Bad	Al	Face-cen cubic	Good	Bi	Rhomb hex	?
C	Tetrag cubic	Bad	As	?	Good			
			Be	?	?	Cd	Hex cl pack	?
Zn	Hex cl pack	?						
			Cr	Body-cen cubic	?	Ca	Face-cen cubic	None
N	Gas	Bad	Mo	Body-cen cubic	?	Mg	Hex	None
O	Gas	Bad	P	Body-cen cubic	Bad			
S	?	Bad	Sb	Rhomb Hex	?			
Co	Face-cen cubic	Bad						
Cu	Face-cen cubic	Bad	Si	Tetrag cubic	Good			
Mn	Very complex	Bad	Sn	Body-cen tetrag	Good			
Ni	Face-cen cubic	Bad	Ti[a]	Body-cen cubic	Bad			
Ir	Face-cen cubic	?						
Rh	Face-cen cubic	?	V	Body-cen cubic	Good			
Pt	Face-cen cubic	?						
			W	Body-cen cubic	?			

[a] According to International Critical Tables (**2,** 453), titanium belongs to class 1

properties.   On the other hand, the elements of class 2 (i e, those that have a tendency to close the gamma loop) have a beneficial effect[14] on the magnetic properties, with the possible exception of phosphorus and titanium.[15]   The insoluble elements, class 3, have little, if any, effect,

[14] See first paragraph of paper
[15] According to International Critical Tables (**2,** 453) Ti belongs to class 1

but in connection with this class it should be pointed out that solubility is a relative term, and that absolute insolubility of one element in another probably does not exist   The statement in regard to the elements of class 3 should be modified therefore, so as to exclude the solubility range, even though this be very small

It is desirable to establish some explanation for the above relationships, i e , to formulate some kind of a statement that will account for all of the observed phenomena   In the attempt to do so it will be assumed that the magnetic properties of iron primarily depend on the regularity of the space lattice

CLASS 1

CLASS 2

Fe+INTERSTITIAL ELEMENTS IN SMALL AMOUNTS

FIG 1

Fe+INTERSTITIAL ELEMENTS IN SMALL AMOUNTS
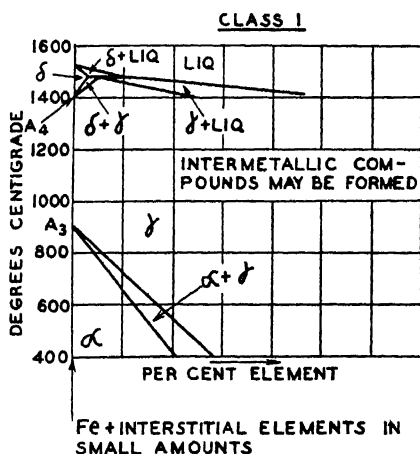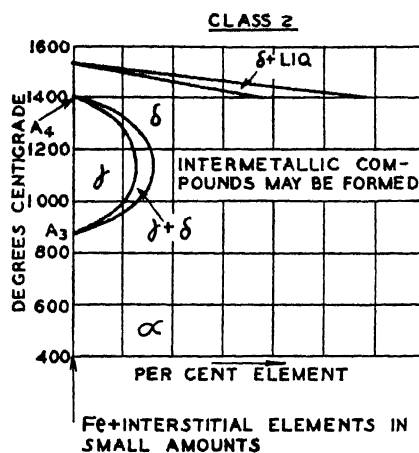
FIG 2

In a recent paper one of the authors[16] made the following statement "The author's present view is that any factor that tends to distort the regular spacing of the atoms in the crystal lattice will cause a decrease in permeability and an increase in hysteresis loss   It matters not whether this factor be impurities in the form of interstitial atoms, strains due to rapid cooling or mechanical working, or interference with the progress of crystallization occurring at the grain boundaries   In most cases all these factors, and perhaps others, combine to give the resultant magnetic properties "

Now, what connection can there be between the position of the allotropic transformation points and the distortion of the crystal lattice?

There are at present two views in regard to allotropy in iron; the orthodox view, that it is an inherent property of iron, attempting no

[16] T D Yensen Does Grain Size Influence the Magnetic Properties of Iron? *Metals & Alloys* (1930) 1, 493

explanation of allotropy, and the recent view suggested by one of the authors[17] that allotropy in iron is due to impurities having characteristics that permit them in small amounts to enter the interstitial spaces of the crystal lattice whereby a strained condition is created such that at a certain temperature range the face-centered lattice (gamma) becomes more stable than the body-centered lattice (alpha), with the result that recrystallization takes place

An increase in the amount of the interstitial elements increases the strain in the alpha lattice and the resulting distortion   A lower kinetic energy (i e , a lower temperature) therefore is required to bring about the transformation   In other words, the interstitial elements distort the alpha lattice and this distortion results in decreased magnetic permeability and at the same time in a lowering of the transformation points   Table 1 shows that the elements that are believed to belong in the interstitial class—boron, carbon, nitrogen, oxygen and sulfur—all belong in class 1, so that the statement above explains part of the classification

The elements of class 2 are mostly substitution elements,[18] that is, they take the place of an iron atom in the space lattice   In so doing there may be some distortion of the lattice, varying with the different elements, but in any case this is believed to be much less than in the case of the interstitial elements and may even be of opposite sign, so as to neutralize partly the effect of the latter   Aside from this possibility, however, the effect of the substitution elements on the magnetic properties and their simultaneous effect on the A_3 and A_4 transformation points may be explained on the basis of the reactions between the substitution elements and the interstitial elements always present to a greater or less extent in iron   Some of the elements of class 2 are known to have great affinity for oxygen, they form stable compounds with oxygen—Al_2O_3, SiO_2, etc —that are precipitated from the solution as slag or else become more or less harmless inclusions   Other elements of class 2, in addition to removing oxygen from solution, may react with other interstitial elements, and the resulting effect on the magnetic properties will depend on the relative distortion produced by the substitution element left in the alloy and by the interstitial elements removed.   In other words, the effect of the elements of class 2 is believed to be due largely to their action in eliminating the interstitial elements from solution   As it must be assumed that the class 2 elements distort the space lattice to some extent, it seems logical to conclude that the smaller the amount needed to eliminate the interstitial elements the better will be the magnetic properties; and, furthermore,

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[17] T D Yensen Pure Iron and Allotropic Transformations   *Trans* A I M E , Iron and Steel Div (1929) 320

[18] Phosphorus probably is not a substitution element and should perhaps be transferred to class 1

that any amount added above that needed to eliminate the interstitial elements will have a detrimental effect on the magnetic properties

Returning now to class 1, consider the elements of and adjacent to the ferromagnetic group cobalt, copper, manganese and nickel. These are substitution elements like the elements of class 2, but differ from the latter in that they do not eliminate the interstitial elements. As they must be assumed to have a distorting effect on the iron lattice without the compensating beneficial effect of the class 2 elements, the resulting effect on the magnetic properties and on the A_3 transformation point may be accounted for [19]

The class 3 elements, being insoluble in iron or nearly so, no effects on the properties of iron should be expected

These considerations may be summarized in the statement that the effect of alloying elements on the magnetic properties and on the allotropic transformations of iron depend directly upon their relative distorting effect on the iron lattice, and indirectly on their reaction with the interstitial elements to form compounds, thus precipitating them from solution

So far the conclusions are only qualitative, but appear sufficiently definite to form a basis for quantitative determinations

DISCUSSION

(Edgar C Bain presiding)

F BITTER, East Pittsburgh, Pa (written discussion) —Both as regards the questions raised in this article, and in the article by Yensen on the allotropic transformation of pure iron,[20] real progress must await definite information concerning the *causes* of phase change. As Dr Yensen stated in his reply to the discussion of the paper just mentioned, his motive in presenting a hypothesis concerning allotropy in iron was to stimulate constructive criticism, and to find a satisfactory explanation of allotropy in pure iron, if such exists. In this connection I should like to make mention of an article by U Dehlinger[21] in which he formulates the problem quantitatively and obtains nice results that eventually may show how to interpret the relationship found by Yensen and Ziegler between magnetic properties and allotropic transformations

Dehlinger starts out with a given sample which shows allotropy, and attempts to interpret it in terms of other properties of the sample. In order to determine at what temperature a given phase change $\alpha \rightarrow \gamma$ will take place it is necessary to know the free energy of the two configurations $F\alpha$, $F\gamma$ as a function of the temperature. The phase which exists at any given temperature is the one having the lowest free energy. A transformation point is therefore characterized by the intersection of the two free energy curves $F\alpha$ and $F\gamma$ (Fig 3). Dehlinger points out that the free energy of a metal is probably largely dependent on the outer electrons. These usually

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[19] The unique properties of the Fe-Ni alloys containing in the neighborhood of 26, 51 and 76 per cent Ni may be accounted for on the assumption that these alloys consist of homogeneous solid solutions corresponding to Fe_3Ni, Fe_2Ni_2 and $FeNi_3$ as already suggested by one of the authors (Reference of footnote 17)

[20] See footnote 17

[21] U. Dehlinger *Ztsch f Physik* (1931) **65**, 535

constitute a degenerate gas whose total energy U and entropy S are independent of the temperature Consequently the free energy as a function of temperature is a straight line

$$F\alpha = U\alpha - TS\alpha$$
$$F\gamma = U\gamma - TS\gamma$$

and $F\alpha$ and $F\gamma$ can cross only once Dehlinger applies these equations to various substances and finds reasonable values for $S\alpha - S\gamma$, the only unobservable quantities For iron, however, where the α phase returns at high temperatures, the theory has to be modified This is an especially pretty aspect of Dehlinger's results From the susceptibility of iron above A_3 Dehlinger concludes that the electrons of the α modification do not constitute a completely degenerate gas This means that $U\alpha$ and $S\alpha$ depend on the temperature, and that therefore $F\alpha$ is no longer a straight line He even attempts to construct a curve for $F\alpha$ using empirical data and finds that $F\alpha$ crosses $F\gamma$ near the empirical A_3 and A_4 points as in the figure It would seem, then, that allotropic transformations in metals are controlled by the outer electrons, and that the reappearance of a phase, as in iron, is dependent on the partial nondegeneracy of the system of valence electrons If data were available on the heats of transformation and the magnetic behavior above A_3 of various iron alloys, it would be possible to calculate their free energy curves as Dehlinger did for iron, and so check his theory by a comparison of theoretical and observed dependence of critical temperatures on the amount and kind of alloying element
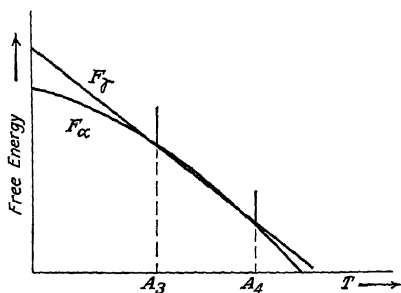
FIG 3

As to the bearing this has on the article by Yensen and Ziegler, it should be emphasized that recent theoretical work by Becker and by myself indicates that hysteresis and permeability in small fields is essentially determined by inhomogeneities in the lattice, and that an alloying element affects these properties chiefly through the distortion it produces, in corroboration of the empirical rule to this effect long ago set up by Yensen and others Taking this in conjunction with the above article, it would seem that the change in free energy of the outer electrons is produced by, or at least accompanies, a mechanical distortion of the lattice This suggestion should be considered in attempts to extend Dehlinger's theory to dilute solutions

A SAUVEUR, Cambridge, Mass (written discussion) —The explanation suggested by the authors to account for the allotropic transformation and magnetic properties of iron appears too highly speculative to be convincing or even alluring Let us consider an alloy of iron and carbon containing some 0 10 per cent of the latter element and let us assume that it is free from impurities After slow cooling, the alloy consists of particles of pearlite embedded in ferrite The authors do not deny that on reheating and upon reaching a certain temperature an allotropic transformation occurs, resulting in a change of space lattice, the iron which had a body-centered cubic lattice now acquiring a face-centered cubic lattice This is generally expressed by stating that alpha iron is converted into gamma iron In order that such allotropic transformation may take place, however, the authors' theory demands that the face-centered cubic lattice of alpha iron be distorted and in the example under consideration this distortion must result from some carbon atoms occupying interstitial positions in the alpha lattice Were it not so, there would be no lattice distortion and consequently no allotropic transformation according to the theory Iron would remain body-centered

at all temperatures   It is also, we are told, upon the distortion produced in the alpha lattice by the presence of carbon interstitially dispersed that the magnetic properties of iron depend

In regard to the assumption that the carbon dissolved in alpha iron is interstitial, this is by no means generally accepted   There are some who believe that in alpha iron the carbon atoms are substituted for some iron atoms   Again let it be recalled that the amount of carbon capable of dissolving in alpha iron at room temperature does not probably exceed some 0 02 per cent   Indeed it has been placed by some at a much lower figure   It also seems probable that the amount of carbon dissolved in alpha iron is independent of the amount of that element present in the alloy   In an alloy containing 0 50 per cent carbon there is no reason to believe that more carbon is dissolved in the alpha ferrite than if the alloy contained but 0 10 per cent carbon   The distortion of the alpha space lattice, therefore, should be the same, hence the magnetic properties likewise, regardless of the amount of carbon present in the steel   However, it is conceivable that the amount of pearlite present would influence the magnetic properties not of the ferrite matrix but of the aggregate as a whole   At any rate, we are asked to accept the assumption that magnetic properties depend primarily upon space lattice distortion, that allotropic transformation depends likewise upon space lattice distortion, that if carbon alone is present the extremely small amount of carbon dissolved in alpha iron occupies interstitial positions, that the resulting lattice distortion explains the magnetic properties of the alloy as well as its allotropic transformation at a certain critical temperature, that the allotropic transformation results from the face-centered lattice becoming more stable at that temperature than the body-centered lattice, all of which involves too much speculation to be readily acceptable

When the alloy under consideration is heated, additional carbon atoms should go into interstitial position and the distortion of the lattice should increase, therefore, with accompanying changes of magnetic properties (decreased permeability?)   In the face-centered (gamma range) the carbon is completely in solution and according to general belief occupies interstitial positions   This should imply marked lattice distortion

If it be argued that the increased distortion or strain resulting from increasing carbon going into solution in alpha iron with increased temperature results finally in the body-centered lattice becoming so unstable that at a certain temperature it transforms into a more stable lattice (face-centered), it is difficult to explain on similar grounds how this face-centered lattice reverts at the A_4 point to a body-centered lattice if it be considered that increasing the temperature of austenite does not result in more carbon atoms going into interstitial position and, therefore, in increased lattice distortion

Assuming now that the alloy contains, besides carbon, which has a "bad" effect upon the magnetic properties, a substitution element like silicon, which has a good effect, the improvement of magnetic properties resulting from the presence of silicon must be due to that element combining with the interstitial element (carbon) and, therefore, eliminating it   More light should be thrown upon the mechanism of such elimination

It is believed that other difficulties might be cited in accepting the authors' theory If these remarks, however, lead the authors to fortify their position and to show that the criticism offered is not sound, they will have accomplished their purpose

YAP, CHU-PHAY, New York, N Y (written discussion) —The subject of allotropy of iron interests me as much as it interests the authors, but my interest, for the present at least, is purely academic

Assuming a complete ignorance of information from other sources, thermodynamics alone can tell us something of the effect of one element on the transition point of iron

(A$_3$)   Thus as shown in my paper,[22] the simple van Laar-Planck equation

$$-\Delta t = \frac{RT_1}{\Delta H_T}(X'\gamma - X'_\alpha) \qquad [1]$$

tells us that when the solute is more soluble in austenite than in ferrite ($x'_\gamma > x'_\alpha$) the transition point will be depressed, vice versa   The question then arises as to why some solutes are more soluble in austenite than in ferrite and others are more soluble in ferrite than in austenite   We might partly subscribe to Hildebrand's conception of the role of internal pressure, but the main difficulty lies in the proper evaluation of the effect of internal pressure not only in the austenite but also in the ferrite   Moreover, I have found many exceptions to the rule regarding internal pressure and solubility in the case of substances with high melting points   At room temperature the influence of internal pressure on solubility relations on, say, aqueous solutions, is undoubtedly important, but it appears to me that such influences become increasingly less important at high temperatures   We may then say qualitatively that when two metals possess certain similar extensive properties (e g , melting points, heats of fusion, crystal habits, etc) they are more likely to be more soluble in each other than in other metals possessing different properties   Thus we may expect a substance crystallizing in the body-centered cubic lattice to be more soluble in another substance crystallizing in the same lattice than in, say, a face-centered cubic lattice [23]

Looking at the problem from another angle, we know from the well-known Clausius-Clapeyron equation

$$\frac{dT}{dP} = \frac{T \, \Delta V}{\Delta H} \qquad [2]$$

that the effect of external pressure is to lower the transition point A$_3$ The effect of external pressure is exactly opposite in the case of the A$_4$ This is, of course, tantamount to saying that an increase in the external pressure would simply lengthen the field in which γFe is stable   Dr Yensen has not defined precisely what he means by lattice distortion, but I infer it to mean, in general, distention of the lattice   Therefore an increase in external pressure should increase the magnetization of iron   Although we have very little experiment on this subject, Ewing[24] found a large increase in magnetization with increasing pressure   The effect of the distention of the lattice can probably be resolved to values related to the temperature coefficient of magnetization   We know that in a fairly strong field the effect of temperature is to decrease the magnetization   On the other hand, since the effect of pressure is to lengthen the field of stability of γFe, the relationship proposed by Dr Yensen between magnetization and allotropy of iron, while interesting, appears to be highly improbable   Moreover, I thought that if Dr Yensen's idea regarding the effect of lattice distention on magnetization is correct, the solute given in class 2 of Wever's classification should contract the iron lattice, but the existing X-ray data do not bear this out

I do not know enough of mathematical physics to know which of the current theories of magnetism is correct   Honda's theory appeals to me because it appears to be consistent with what I know regarding metals and I have a great admiration for his various studies in metals   I think, as Mr Corson once pointed out in discussing a paper presented before this Institute, it is better to leave to future generations of mathematical physicists the formulation of well-founded theories   In the meantime, however, we might profitably adopt the empirical methods of investigations

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[22] A I M E Tech Pub 381 (1931)   (Abstract on page 141)

[23] Eventually this problem will be solved, I think, by the method of calculating the lattice energetics after the method of Born and his pupils

[24] Quoted from K Honda Magnetic Properties of Matter, 53   Tokyo, 1928 Syokwabo & Co

Two years ago in my discussion of Dr Yensen's paper on allotropy of pure iron, I pointed out that the problem could perhaps be studied with more profit by thermodynamics   Since I expect to publish a paper on the subject in the very near future I shall confine myself to a few remarks on the method of approach to the study of the problem   On account of the reversible polymorphism, the entropy curves of γFe must intersect the entropy curve of αFe [25]   This is due to the fact that since the entropy change, $\Delta S = \Delta Q/T$, where ΔQ is the heat of transition and T the temperature of transition, the entropy of γFe is larger than the entropy of αFe at 900° C , but at

1400° C the reverse is true   It is for this reason that the two entropy curves must intersect each other as shown in Fig 4   The only way we can conceive of the absence of the reversible allotropy is when the two entropy curves do not intersect at all   This does not, however, totally rule out the presence of one allotropic transformation point, in order to conceive the complete absence of allotropy in iron, one must first assume that the free energy (F) curves which can be derived from Fig 4 do not intersect each other up to the melting point of iron   Having pointed out the theoretical conditions under which the allotropy of iron might conceivably be

FIG 4 —THE ENTROPY CURVES OF α AND γFE BETWEEN THE A_3 AND THE A_4 POINT.

suppressed, it remains to indicate the experimental methods by which we may ascertain whether or not it is actually possible to do so   Since we know that $S = C_P \ln T$, or better still, $dS/dT = C_P/T$, a complete knowledge of the various heat capacities involved should form a more logical basis of the study of this interesting problem

J S MARSH, New York, N. Y —Before reading my discussion, I should explain an apparent divergence with Dr Bitter's discussion   Dr Bitter, as those of us know who have been attempting to follow the rapid movement in contemporary physics, is one of the champions of Zwicky's mosaic structure theory   Unless I misunderstood the tenor, he talked about blocks containing possibly 10^5 atoms, and I have attempted to get at something on a much smaller scale

(Written discussion) —It is always a pleasure to read Dr Yensen's papers on magnetic properties, for there is always assurance that the findings represent skilful technique coupled with the guidance of theory in a difficult field

Although it is difficult to steer clear of inferences from contemporary physics when the subject matter is considered (and the magnitude thereof is perhaps belied by the brevity of the paper) it seems best to do so, in keeping with the authors' deliberate avoidance of that phase   It is the purpose of the comments to follow to amplify when amplification seems desirable

It is known that the effect of an alloying element on the transformation points of iron depends on its relative solubility in α and γ iron   Inspection of Table 1 shows (as has been noted before) that the "loop-forming" elements are predominantly body-centered cubic, and that the "loop-opening" elements are predominantly face-centered cubic   This suggests immediately that more must be known about the mechanism of solubility   This thought is furthered by examination of atomic volumes For example, the atomic volumes of Ni, Cr, and Fe are 10 9, 11 9, and 11 6 Å, respectively, yet Ni decreases A_3 and Cr either increases or has no effect on A_3 Further-

[25] Consult, for example, Tammann The States of Aggregation   (Trans by Mehl) New York, 1925   D Van Nostrand Co

more, the Si atom is smaller than, and the V atom is larger than, the Fe atom and both increase A₃.

Examination of the elements which have a beneficial effect on the magnetic properties of iron from the standpoint of "normal" metallic elements shows them to be predominantly "abnormal" This is again suggestive, and again indicates the necessity of better understanding of just what takes place when two or more atoms interact The problem is complex, but advances are being made daily And so, the purpose of this amplification is to remind that a purely mechanical picture of distortion must not be constructed

F R HENSEL, East Pittsburgh, Pa —Dr. Yensen asked me to report a few experimental facts which we found in an investigation recently started at the Westinghouse Research Laboratories to study the temperature and dilatation of pure iron at the A₃ point

We have used the Chevenard industrial thermal analyzer As test material Armco iron and a pure iron containing approximately 99 98 per cent Fe are being used The tests are being run in H₂ atmosphere The test materials were heated in hydrogen at 1400° C for about 12 hr before testing It was hoped to remove all traces of oxygen by this treatment. The gas analysis is being made by Mr Ziegler and is not yet available

We have not found that the A₃ point disappears It is just as strong in the purest sample as in a material containing considerable amounts of oxygen However, one thing was interesting in investigating Armco iron While in an as-received Armco sample tested in air atmosphere the Ac₃ point starts at 900° C , in the same sample annealed 12 hr at 1400° C the Ac₃ point is raised to 935° to 945° C The temperature-time curve of the standard sample shows a sharp indentation at the Ac₃ point in the latter case which was not noticeable before

This seems to point to the fact that actually the Ac₃ point occurs at a higher temperature than is generally accepted The impurities undoubtedly are the reason for the lowering of the Ac₃ point of commercially pure iron, but I do not believe that they alone are responsible for transformations of pure iron as such Thermodynamical considerations will show that the free energy curves of alpha and gamma iron as shown by Dr Bitter will always intersect The temperatures where they intersect, however, will be greatly influenced by certain impurities

F WEVER, Dusseldorf, Germany (written discussion*) —I wish to thank Dr Yensen and Dr Ziegler for stating that the classification proposed by me for the alloying elements of iron according to their effect on the polymorphic transformations also might find a remarkable parallel in the effect on the magnetic properties I agree with the authors that the internal causes of the properties that place an element in one class or another must, as they say, be found in a disturbance of the lattice which takes place on the formation of the alloy or, as I have stated, in the comparative size of the radius of the atom which decides whether the element will enter the lattice space of the iron or whether it forms a substitution mixed crystal, and the magnitude of the lattice disturbance thus caused However, I cannot follow the authors when they regard as proof for the idea brought forth by Dr Yensen the fact that pure iron is not allotropic and this is caused only by impurities with interstitial elements I still prefer to remain "orthodox" at the present time and repeat the opinion that I have given elsewhere that we must wait for the direct proof of the accuracy of the Yensen idea, which may be brought forth by investigation of the purest iron

T. D YENSEN AND N A ZIEGLER (written discussion) —Professor Sauveur thinks that our explanation of the relationship between allotropy and magnetic properties

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* Translated from the German

is too speculative to merit serious consideration   It should be noted that we have proposed a hypothesis which by definition is an explanation based on speculation   It serves the purpose of systematizing unrelated data until they are either confirmed or disproved by further experimental facts   We also hoped to bring out possible explanations of allotropy based on accepted theories of matter and thus to remove it from the list of so-called "inherent" or unrelated properties   Allotropy so far has been in much the same category that magnetism was in up to the time when the suggestion was made that it is due to electricity in motion   This hypothesis having now been confirmed by experiments, magnetism is no longer simply an "inherent" characteristic, it is based on more fundamental properties—the properties of spinning electrons

We have already received a contribution to our paper that offers a possible explanation of allotropy   Dr Dehlinger, as Dr. Bitter has pointed out, suggests that allotropy may be connected with free energy in such a way that the face-centered cubic lattice may be the more stable structure between the A_3 and the A_4 transformation points   Furthermore, the intercept of Dehlinger's two curves may very well depend on the amount of impurities in the iron; and the question whether pure iron has or has not allotropic transformations on the basis of Dehlinger's results will depend on whether his two curves, the one for body-centered and the one for face-centered cubes, do or do not intersect as the impurities approach zero   Dr Esser in Aachen and Dr. Hensel in Pittsburgh have both found appreciable increases in the A_3 point as the degree of purity increases, Dr Hensel reporting a value as high as 950° for the A_3 point by repeated hydrogen treatment of the purest iron available

As to the question whether carbon dissolved in iron is interstitial or not, we have Dr Westgren's experimental results as evidence that it is interstitial, and no evidence to the contrary   This brings up another very interesting point   The solubility limit for carbon in iron is based on microanalysis in connection with analysis for total carbon   In a recent paper,[26] one of us pointed out that this probably leads to too high solubility   The smallest precipitates of Fe_3C that can be detected at 5000 dia   contain about one million atoms, and the largest part of the carbon content undoubtedly is represented by particles that are smaller than that invisible under the above magnification   We may call them colloidal   According to Westgren, the smallest conceivable particle of Fe_3C would contain 4 atoms of carbon and 12 of iron   This being the case, the actual solubility may be much less than that previously assumed, namely, 0 006 to 0 008 per cent   This, however, does not alter the argument as far as the effect on the lattice distortion is concerned, as these small colloidal precipitates situated in the lattice certainly would distort it even more than the corresponding amount of atomic carbon   As pointed out in the paper referred to, this precipitate may actually be what causes magnetic and other aging in iron

Referring again to Dr Sauveur's discussion, it is clear that the amount of carbon actually in solution in alpha iron will be zero for no carbon present and will increase to the maximum solubility as the total carbon content increases and will remain constant at this value for higher carbon contents

The suggested increased lattice distortion in gamma iron as carbon goes into solution does not seem to have any direct connection with our hypothesis   Furthermore, our statement in regard to the "good" effect of silicon apparently was misunderstood by Professor Sauveur.   The good effect is assumed to be due to silicon combining with oxygen to form SiO_2 and not with carbon

Although we cannot agree with Professor Sauveur in all his statements, we are glad to have him point out possible weaknesses in our presentation

[26] T D Yensen Effect of Impurities on Ferromagnetism   Amer. Physical Soc., Schenectady Meeting, Sept 1931.

We thoroughly agree with Mr Marsh that the subject of allotropy in iron should be studied on the basis of contemporary physics, as already pointed out, and any suggestion along this line that has a bearing on the subject will be gratefully received Mr Marsh's references to the mechanism of solubility and to interaction between atoms are, we think, decidedly relevant

Mr Yap again contributes to the discussion of allotropy by means of thermodynamics and physical chemistry, as was done earlier by Dr Anson Hayes Such contributions are valuable, as the final results must necessarily be in accord with these accepted and thoroughly tested laws and principles However, numerical calculations require experimental data, and the results of such calculations are less reliable than the experimental data, because errors are apt to be accentuated when used in extrapolation, no matter how reliable the laws are that are used in this extrapolation For a long time we have been familiar with the sensitivity of the magnetic properties to impurities We have found that impurities, in amounts measurable only by extraordinary means, have the most profound effect on the magnetic properties. We are just beginning to get an indication of the effect of minute amounts of impurities on the allotropic transformations While thermodynamics and physical chemistry can give us the tendency in regard to the effect of impurities on allotropy, we should be very careful in the use of present experimental data, as it is almost certain to lead to erroneous results

In regard to what we mean by lattice distortion, we do not, as Mr Yap assumes, confine ourselves to "distention of the lattice," but intended to include *irregular* displacements of the atoms in the lattice and *irregular* changes in the lattice angles The point at issue may be stated this way (as was done by Dr Bitter)

Mr Yap takes exception to our notion that phase changes are influenced by distortions of the lattice, and prefers to speak of free energy and entropy The difference is entirely one of point of view When a kinetic theory of metals is developed, the free energy, etc , must necessarily be derived from the positions and motions of the constituent atoms and so distortions of course will influence the thermodynamic potentials It should further be emphasized that such detailed kinetic theory considerations are a valuable supplement to thermodynamic methods, as the development of the gas theory, for instance, has shown

It should be noted that, contrary to Mr Yap's statement, pressure has only a slight effect on the magnetization of iron and that the change is a decrease (not an increase), as shown by Honda [27] On the other hand, tension increases the magnetization for low magnetizing forces (Honda's Figs 42 and 43) while compression has the opposite effect

Mr Yap's point in regard to the effect of pressure on magnetization and its relationship to the "field of stability of gamma iron" must be disregarded, therefore, because it is based on faulty premises

As far as Honda's theory of magnetism is concerned, it suffers from at least one serious difficulty, namely, that it does not account for the effect of temperature on magnetization, as Honda's magnetons are supposed to reside in the nucleus, and the state of the nucleus is unaffected by temperature

The remainder of Mr Yap's discussion is closely related to the approach to the problem by Dehlinger as given by Dr Bitter in the discussion of our paper This sort of approach looks promising and we shall welcome further contributions by Mr Yap along this line

We appreciate Dr. Wever's remarks and his "watchful waiting" attitude towards our hypothesis The only other attitude that would be justified at present would be an experimental attack, and we should naturally welcome a contribution by such an eminent metallurgist as Dr Wever

[27] K. Honda *Op cit* , 61, Fig 57

Dilatometric Study of Chromium-nickel-iron Alloys

By Vsevolod N Krivobok* and Maxwell Gensamer,† Pittsburgh, Pa

It is generally recognized that "low temperatures" have a definite effect on the properties of metals and alloys. Furthermore, it is also generally understood that the effect is decidedly adverse The possibility that the same low-temperature treatment might be employed for the purpose of improving certain properties of the alloys has received less attention until recently, and the experimental and theoretical knowledge consequently is meager. The effect of low temperatures may be studied in two ways. by studying such properties as tensile strength, hardness, impact resistance, etc , at low temperature, and by studying the properties of alloys at room temperature *after* these alloys have been subjected to a low-temperature treatment. Even in the latter case, certain properties will differ materially from the same properties obtained on identical material but without cold treatment. In other words, subjecting alloys to cold treatment results in an irreversible change in mechanical properties Changes of this character are usually indications of the appearance of a new phase or phases, and would be likely to occur in alloys which, either by virtue of their composition or by heat treatment, are retained at room temperature in a metastable condition. Consequently, studies of the effect of low temperatures logically should be conducted from the physicochemical point of view, since the results of such studies not only would furnish metallurgists with interesting theoretical data but would clearly indicate the classes of alloys that would hold promise of improvement, and, possibly, of new applications.

As the present investigation deals with chromium and chromium-nickel alloys of iron of the stainless variety, it has been thought desirable to present the data concerning low-temperature properties of these alloys, available from the most recent and most comprehensive work of H. S. Russell [1] A summary of these data is given in Table 1. The data are confined to a limited number of alloys of the type dealt with in the present

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† Assistant Metallurgist, Bureau of Metallurgical Research, Carnegie Institute of Technology

[1] Symposium on Effect of Temperature on Properties of Metals Amer Soc Test Mat (1931) 486

TABLE 1.—*Summary of Data from Work by Russell*[a]

Composition and Treatment

Reference No	Carbon, Per Cent	Chromium, Per Cent	Nickel, Per Cent	Treatment
4	0 07	13 9	0 1	Annealed.
4-H	0 07	13 9	0 1	Quenched and drawn
6	0 09	17 5	9 2	Annealed

Tension Test Results

	Tensile Strength		Elongation in 2 In , Per Cent		Reduction in Area, Per Cent	
	Room Temp	−40° C	Room Temp	−40° C	Room Temp	−40° C
4	66,000	75,400	40 2	45	75 8	72 9
4-H	123,000	130,000	22 5	25 2	65 9	66 8
6	88,000	160,000	69 9	48 7	76 7	70 2

Brinell Hardness Test

	Room Temp	0° C	−20° C	−40° C	−60° C	−75° C
4	139	143	148	148	154	155
4-H-1	215	227	230	237	241	246
4-H-2	270	273	282	284	289	299
6	144	156	171	183	193	192

Charpy Impact Resistance, Ft-lb

	Room Temp	0° C	−20° C	−40° C	−60° C	−80° C
4	39	38	4	25	1	1
4-H	28			3 25		
6	80	80	77	6 78	81	82

[a] Reference of footnote 1.

work. For the present investigation, a larger number of alloys, with a systematic variation in composition, was secured. Their analyses are given in Table 2 A study of various properties of these alloys at low temperatures and as affected by low temperature is under way. Such a study, as is well realized, is not only momentous in scope but is not devoid of considerable difficulties. Consequently, as a preliminary step, it was decided to ascertain the effect of low temperatures on some property at room temperature, in order merely to indicate those alloys in which physicochemical changes could be brought about by cold treatment.

The property chosen for this purpose was hardness as measured by the Rockwell hardness tester.

TABLE 2.—*Analyses of Alloys Studied*

Alloy No	Carbon, Per Cent	Chromium, Per Cent	Nickel, Per Cent
571	0 04	15 29	
576	0 44	17 78	
572	0 05	17 40	1 98
694	0 17	17 11	2 20
1–577	0 27	18 42	2 00
20	0 31	16 80	2 20
27	0 34	16 68	2 25
24	0 37	20 45	2 10
28	0 43	17 48	2 45
577	0 60	18 15	1 97
573	0 05	17 43	3 99
8	0 34	17 53	4 20
31	0 41	17 38	4 20
578	0 84	18 31	3 46
18–5	0 10	17 60	5 08
695	0 16	17 72	4 16
1-578	0 25	18 66	4 24
1-574	0 05	17 20	7 82
9	0 23	17 84	8 00
16	0 34	17 56	8 10
18-8-01	0 01	18	8
Commercial	0 13	18	8
635	0 05	17 81	11 40
5	0 20	18 02	11 95
575	0 22	16 55	10 65
15	0 31	18 08	11 70
23	0 42	16 50	11 80
693	0 18	17 26	

Some of the alloys investigated were quenched from various temperatures, while others were allowed to air cool, since such treatments are likely to be encountered in practice. The quenching treatment had as its object the retention of the material in the austenitic condition. It was found that while the temperature at which this could be accomplished varied, depending upon the composition of the alloys, a temperature of 1260° C. (2300° F) was effective for all the alloys in which austenite could be retained at all. Subsequent to quenching, the alloys were immersed either in a mixture of solid carbon dioxide and acetone, or in liquid nitrogen, for from ½ to 12 hr. The data on the hardness of the alloys before and after immersion are summarized in Table 3. The change in hardness in certain cases is worthy of attention. No attempt was made to obtain, by this method, the maximum increase in hardness. The

TABLE 3 —*Rockwell Hardness of Alloys before and after Immersion*

Alloy No	Air-cooled, 1850° F	Air-cooled, 1850° F and Cold-worked	Water-quenched, 1850° F	Water-quenched, 1850° F and Cold-worked		Air-cooled, 2300° F	Air-cooled, 2300° F and Cold-worked	Water-quenched, 2300° F	Water-quenched, 2300° F and Cold-worked	
				CO2	N2				CO2	N2
571								90B	94B	93B
576	39C	41C	45C	41C		24C	49C	30C	57C	54C
572		17C	22C							26C
694								32C		31C
1-577			44C	48C	51C			37C	46C	48C
20			46C	50C	50C			26C	51C	52C
27	49C	48C-N2				27C	50C-N2	27C	50C	
24			45C	43C	51C			23C	24C	23C
28	35C	40C-N2				14C	16C-N2	94B	94B	94B
577	58C	58C-N2				31C	57C-N2	21C	38C	44C
573								101B	26C	28C
8	35C	40C-N2				10C	16C-N2	86B	92B	95B
31								93B	93B	93B
18-5	35C	43C				28C	41C-N²	17C		37C
695	22C	28C	26C	28C		20C	36C	14C		35C
1-574								76B	88B	94B
9								77B	85B	85B
16								86B	85B	83B
635								71B	72B	70B
5								79B	81B	78B
575								76B	78B	78B
15								81B	82B	82B
23			95B	96B				82B	85B	83B
693								49C		49C

quenching temperature of 1260° C. is not the proper temperature for some of the alloys, consequently, it is to be expected that further increases in hardness may be obtained through careful selection of a heat-treating procedure

It is not intended to discuss here the possibilities that may be offered by the change in mechanical properties as indicated by the figures for hardness, but to present these preliminary data for the consideration of those who may find them suggestive.

To secure data that would provide an explanation of the causes of the changes in mechanical and other properties, in other words, to study the course of the phase change, the dilatometric method was selected. When applied to some other work this method proved to be sufficiently sensitive and accurate and, furthermore, to be capable of directly following the progress of the transformation. This work has been carried out in two ways: (1) by cooling a quenched sample from room temperature to that of liquid nitrogen; (2) by making a complete dilato-

metric run between the temperature of liquid nitrogen ($-190°$ C, $-310°$ F) and $1000°$ C ($1832°$ F)   Only a condensed description of the method of procedure and the apparatus is presented, since the details can be obtained in another recent publication [2]

APPARATUS

The dilatometer used for the first part of this investigation is an exceedingly simple one.   It was adapted from the Bureau of Standards design [3]   The specimen rests on a short piece of quartz tube, in the bottom of a closed-end quartz tube 18 in. long   On top of the specimen is another quartz tube (small enough in diameter to move freely within the outer closed-end tube) which transmits the dilatation of the specimen to a dial gage head   The dial is connected by a lug on its back to the outside quartz tube by the same device described by the Bureau of Standards.

The specimens were cylinders about $\frac{1}{2}$ in in diameter and only 1 in long.   It is realized that this is too short to give a reliable figure for the coefficient of thermal expansion, since the dial used reads to only 0 0001 in and is not accurate to more than 1 per cent   The short specimen was adopted to minimize the effect of the temperature gradient which undoubtedly exists.   No attempt to measure the coefficient of thermal expansion accurately was made, so the spherical seating arrangement used at the Bureau of Standards was eliminated, and the ends of the cylindrical specimens were machined plane on the seating surfaces, but with a boss fitting the inside diameter of the quartz tubes to facilitate centering of the assembly.

The thermocouple was attached directly to the specimen by pounding the bead into a saw cut in its upper end   The thermocouple wires were run through a refractory insulating tube up the inside of the quartz tube transmitting the movement to the dial gage, brought out through holes in a brass cap which provided the surface for the "feeler" of the diagage, and then to a "cold" junction at room temperature.   The electromotive force of the thermocouple was measured with a type K potentiometer   The couple was calibrated by direct immersion in liquid nitrogen, and at intermediate temperatures by comparison with a pentane in glass thermometer, using acetone cooled by solid carbon dioxide.

Observations of the dial gage head reading at selected values of thermocouple electromotive force were made by gradually raising a Dewar flask containing liquid nitrogen up around the dilatometer assembly, finally immersing the closed-end outer tube to a depth of 2 or 3 in. above the top of the specimen.   The heating run was made by dropping the

[2] F M Walters and M Gensamer A Dilatometric Study of Binary Iron-Manganese Alloys   Trans. Amer. Soc. Steel Treat (1931)

[3] P Hidnert and W T Sweeney. Thermal Expansion of Magnesium and Some of Its Alloys.   U. S Bur. Stds Jnl. of Research (1928) 1, 771.

Dewar flask, the ice formed by condensation on the cold tube preventing too rapid heating. Observations were made at 0 1 millivolt intervals, corresponding to from about 1 5° C to 2 0° C. intervals.

The runs from −190° to 1000° C were made in a dilatometer described in the paper by Walters and Gensamer [4] The dilatometer is identical with the one described above, but is arranged so that the heating can be conducted *in vacuo* or in an inert gas atmosphere. The runs described in this paper were made *in vacuo*. The rate of heating and cooling was carefully controlled by raising or lowering the furnace current a definite and small amount every one or two minutes, so that a uniform rate was maintained. The normal rate was about 12° C per minute over most of the range, and somewhat less than this at low temperatures   About 1½ hr was consumed in heating from 0° to 1000° C , and the same for cooling   To maintain this rate on cooling, it was necessary to drop the furnace away from the dilatometer when near room temperature   This effect of this change in rate has not been detectable   The procedure for low temperatures has been described   When reading the dial it was found desirable to jar the table supporting the assembly, this aided materially in getting smooth curves   Length readings were taken at intervals of 1 mv , which represented about 12 5° C   Individual observations have not been indicated on the curves, because a complete run meant at least 85 observations   In very few cases have individual observations been further away from the curve as plotted than 0 01 per cent. The dilatation of the quartz can be neglected, since the dilatometer is differential in principle and the thermal expansion of quartz is small compared to that of steel.

EXPERIMENTAL RESULTS

Quenched Alloys Cooled from Room Temperature to −190° C.

Alloys of Stainless Type (14 to 18 Per Cent Chromium).—The dilatometric curves for the three alloys of this group are given by tests 1 and 3 in Fig. 1. The dilatation of the low-carbon, 15 per cent chromium alloy (No 571; test 1) is regular, with no indication of any phase change Consequently, the low-temperature treatment should not result in any change in mechanical properties when the alloy is returned to and tested at room temperature. It should be understood, however, that the properties of the alloys *at* low temperature may not remain the same. An alloy with carbon between 0.40 and 0.50 per cent and no nickel shows marked dilatometric change, as is depicted in test 3, Fig. 1. The experiment on this particular sample was one of the first performed and was continued only to the temperature of solid carbon dioxide in acetone, which is approximately −70° C. At this temperature the phase change is not completed, consequently the sample should have been taken to a

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[4] F. M. Walters and M Gensamer· *Op. cit.*

lower temperature   The treatment given the alloy, however, was sufficient to result in a remarkable increase in hardness   Again, as in the case
of other alloys, it remains to be ascertained how other physical properties
are changed, especially impact resistance and corrosion resistance
Incidentally, cooling of this sample to the temperature of liquid nitrogen
instead of to that of solid carbon dioxide does not have further effect on
its hardness, as is evident from Table 3

Alloys of General Composition of 18 *Per Cent Chromium and* 2 *Per Cent
Nickel* —No phase change, it will be remembered, was observed in
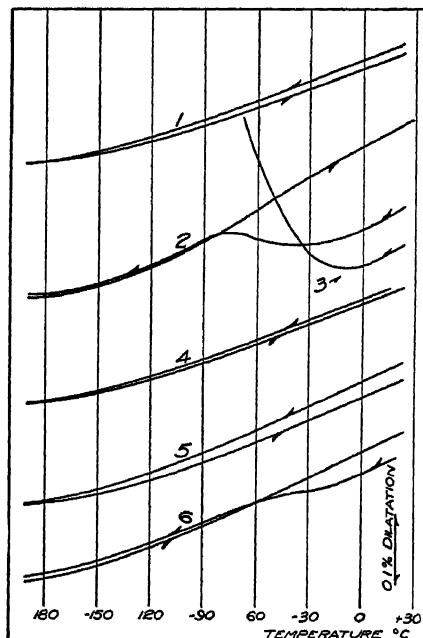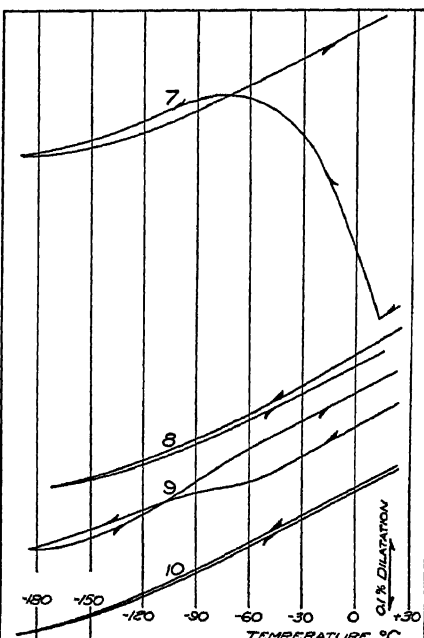
<table>
<tr><td align="center">FIG 1.</td><td align="center">FIG. 2</td></tr>
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FIG 1 —TEST 1, ALLOY 571 (0 04 PER CENT C, 15 3 CR, 0 NI)
          TEST 3, ALLOY 576 (0 44 PER CENT C, 17.8 CR, 0 NI)
          TEST 4, ALLOY 572 (0 05 PER CENT C, 17.4 CR, 2 0 NI).
          TEST 5, ALLOY 694 (0 17 PER CENT C, 17.1 CR, 2 2 NI)
          TEST 6, ALLOY 1-577 (0.27 PER CENT C, 18 4 CR, 2 0 NI).
FIG 2 —TEST 7, ALLOY 20 (0 31 PER CENT C, 16 8 CR, 2 2 NI)
          TEST 8, ALLOY 20, SECOND RUN.
          TEST 9, ALLOY 24 (0 37 PER CENT C, 20 4 CR, 2 1 NI).
          TEST 10, ALLOY 24, SECOND RUN

chromium alloys containing very little carbon (alloy 571 and others).
The same is true of a similar alloy to which approximately 2 per cent of
nickel was added (alloy 572).   A dilatometric curve reproduced in test 4,
Fig. 1, shows no irreversible volume change.   There is noticed a slight
increase in hardness of the alloy after cold treatment, but this increase
is rather insignificant.   The same is true of an alloy with 2 per cent nickel
and 0.17 per cent carbon (alloy 694), the dilatometric curve for which is

reproduced in test 5, Fig. 1. With an increase in carbon content to 0 27 per cent (alloy 1-577) the composition of the alloy is such that the retention of austenite is possible, as may be seen from test 6, Fig 1, consequently the hardness may be changed by cold treatment.

An alloy next in line as far as carbon content is concerned (alloy 20, containing 0 31 per cent carbon) presents an anomaly from the point of view of the magnitude of phase change (test 7, Fig 2) as compared with the preceding alloys It may be explained on the ground of somewhat lower chromium content because it was observed that as the chromium
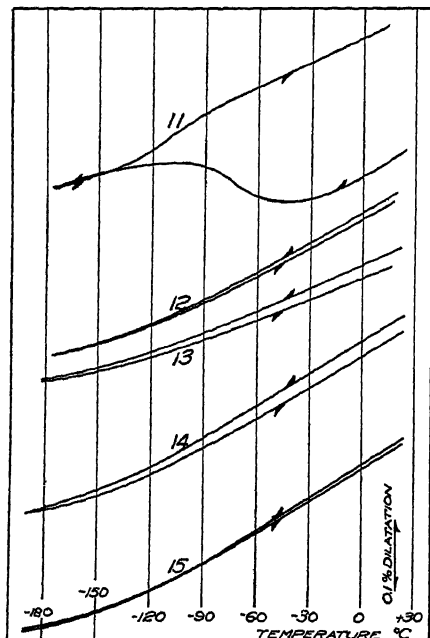
FIG 3.

FIG 4.

FIG 3.—TEST 11, ALLOY 577B (0 60 PER CENT C, 18 2 CR, 2 0 NI)
TEST 12, ALLOY 577B, SECOND RUN.
TEST 13, ALLOY 573 (0 05 PER CENT C, 17 4 CR, 4 0 NI)
TEST 14, ALLOY 31 (0 41 PER CENT C, 17 4 CR, 4 2 NI)
TEST 15, ALLOY 578 (0 84 PER CENT C, 18 3 CR, 3 5 NI).
FIG 4 —TEST 16, ALLOY 18-5A (0 10 PER CENT C, 17 6 CR, 5 1 NI)
TEST 17, ALLOY 18-5B, ANOTHER SPECIMEN.
TEST 18, ALLOY 18-5B, SECOND RUN.
TEST 19, ALLOY 695 (0.16 PER CENT C, 17 7 CR, 4 2 NI).
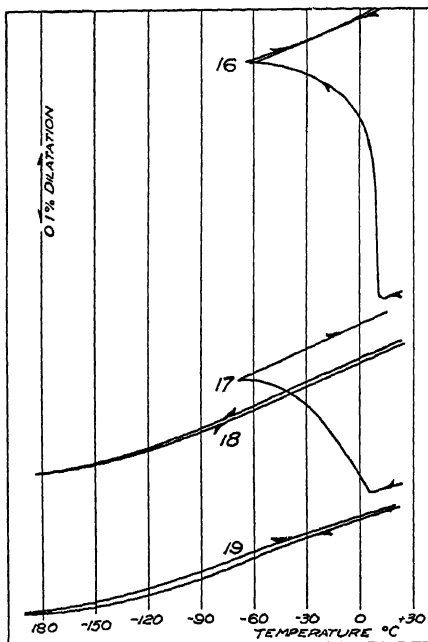
content increases the magnitude of the volume change decreases; this is seen from a comparison of alloy 20 and alloy 24 The hardness of alloy 20 changes remarkably when the cold treatment is applied, changing from 26 Rockwell C to 52 Rockwell C, although as the quenching temperature is lowered the effect of cold treatment is much less pronounced. A similar observation was made in other cases as, for example, alloy 27. To test the completeness of the transformation and to obtain normal

heating (that is, up to room temperature) and cooling curves, a second dilatometric run was carried out immediately after the observation just discussed, no further irreversible dilatation was observed (test 8, Fig. 2). The 0.37 per cent carbon (tests 9 and 10, Fig. 2) and 0 60 per cent carbon (tests 11 and 12, Fig 3) alloys (24 and 577) behave similarly, although the magnitude of the transformation, as indicated by both dilatation and hardness tests, was considerably less.   The intermediate carbon alloy, 0 37 per cent, showed surprisingly little increase in hardness and dilatation.

Alloys of General Composition of 18 *Per Cent Chromium and* 4 *Per Cent Nickel* —This group, containing 0.05 per cent carbon (alloy 573, test 13,
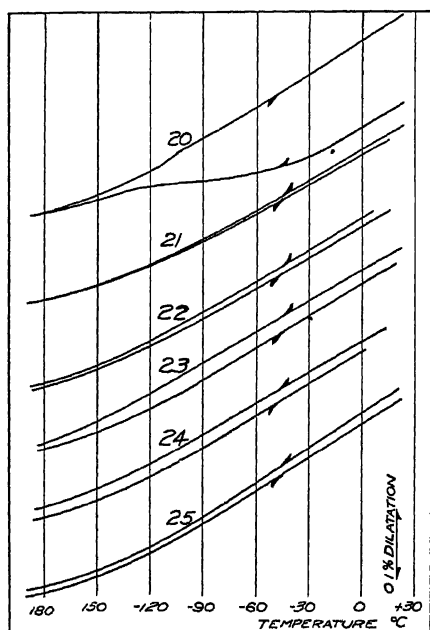
FIG. 5.   FIG 6.

FIG 5.—TEST 20, ALLOY 1-574 (0 05 PER CENT C, 17.2 CR, 7 8 NI).
TEST 21, ALLOY 1-574, SECOND RUN.
TEST 22, ALLOY 1-574, QUENCHED AND COLD-WORKED
TEST 23, ALLOY 9 (0 23 PER CENT C, 17.8 CR, 8 0 NI)
TEST 24, ALLOY 635 (0 05 PER CENT C, 17 8 CR, 11 4 NI).
TEST 25, ALLOY 575 (0 22 PER CENT C, 16.6 CR, 10 7 NI).
FIG 6.—TEST 26, ALLOY 20 (0 31 PER CENT C, 16 8 CR, 2.2 NI).
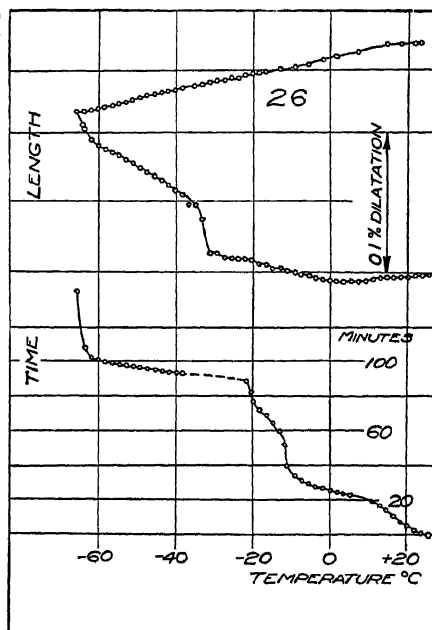
Fig 3), 0 16 per cent carbon (alloy 695, test 19, Fig 4), 0.41 per cent carbon (alloy 31, test 14, Fig 3), and 0.84 per cent carbon (alloy 578, test 15, Fig 3) show no irreversible dilatation with cold treatment.   A 0 10 per cent carbon alloy containing 5 per cent nickel (alloy 18-5, tests 16, 17 and 18, Fig 4), however, shows a remarkable transformation and considerable hardness change [5]

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[5] The experimental results were confirmed several times   A study of this alloy from a different angle may be necessary before the observed anomaly can be explained

Alloys of General Composition of 18 *Per Cent Chromium and* 8 *Per Cent Nickel.*—Commercial "18-8" containing 0.13 per cent carbon has been subjected to quenching and cold treatment and shows no transformation An 18-8 alloy containing 0 05 per cent carbon, however, shows considerable dilatometric irreversibility (alloy 1-574, tests 20 and 21, Fig 5), thus corroborating the evidence gathered from the hardness tests.   In order to establish that the change was not due to any cold work which the specimen had received in the process of machining, a sample was quenched and then severely cold-worked by hammering, after which a dilatometric run to −190° C was made (test 22, Fig 5).   No transformation was observed, which indicates that the effect of severe working was to induce and apparently to complete the phase change at room temperature, with the result that no further transformation is to be obtained on immersing in liquid nitrogen

A 0 23 per cent carbon alloy (alloy 9, test 23, Fig. 5) showed no dilatometric effect

Alloys of General Composition of 18 *Per Cent Chromium and* 11 *Per Cent Nickel.*—The 0 05 per cent carbon (alloy 636, test 24, Fig 5) and the 0 22 per cent carbon (alloy 575, test 25, Fig 5) alloys show no dilatometric irreversibility

Dilatometric Observation from 1000° *C. to* −190° *C.*

It is to be anticipated that the process of phase change induced by cold treatment in the alloys containing metastable austenite retained by quenching is essentially similar to one occurring on slow cooling   In important details, however, the two are far apart. the temperature of the transformation, the magnitude of the transformation, etc., may differ considerably.   Furthermore, a complete run employing a slower rate of cooling may reveal other phenomena which are not observable with the first method used in this investigation.   Consequently, a number of steels, representative of various types of chromium-nickel alloys, were selected from available material for complete dilatometric runs   The selection was made so that the effect of carbon and nickel on iron-chromium alloys, containing approximately 18 per cent chromium, could be studied.   A description of the results of these dilatometric tests follows For convenience, the dilatometric runs on each alloy, where more than a single heating and cooling curve was necessary, are numbered in the order in which they were performed   Also, in the subsequent discussion, the terms "positive deviation" and "negative deviation" will be used, since it is believed that such terms are the simplest and yet most descriptive. Positive deviation shall mean a deviation from the normal thermal expansion or contraction curve in the direction that would result in an expansion if the magnitude of the dilatation were sufficiently greater than the normal dilatation over the s ime temperature range.   Similarly, a negative devia-

tion shall mean a deviation that would result in a contraction.   When the magnitude is not sufficiently great and opposed to the normal rate, or where it is additive to the normal rate, it is manifested by a change in slope

Alloy 571 (0 04 per cent C, 0 per cent Ni, 15 3 per cent Cr; test 27, Fig 7) —This alloy belongs to the general type of stainless irons   On the first heating (run 1), two negative deviations were unexpectedly observed.   On cooling (run 2), a positive deviation occurred just below 300° C , extending over a temperature range   Subsequent heating runs
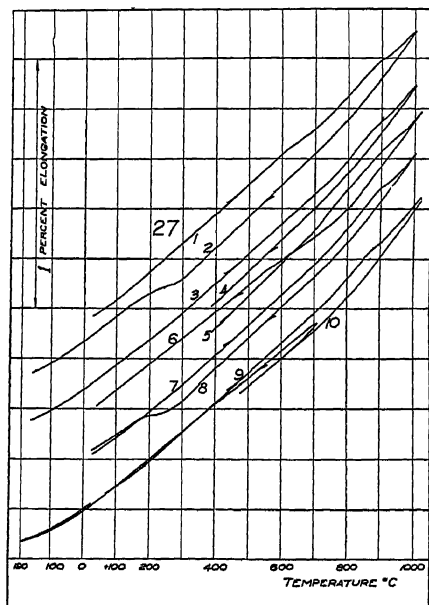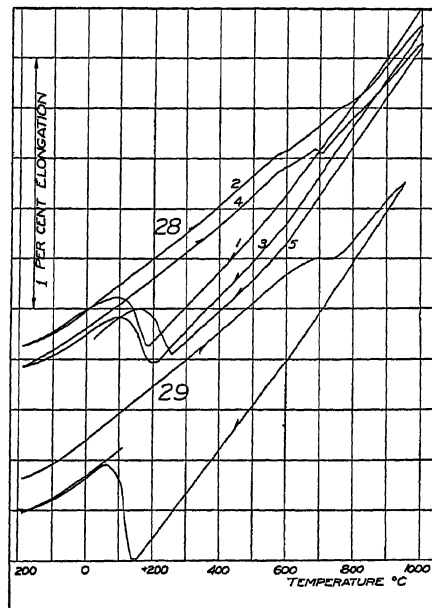
FIG 7.   FIG. 8

FIG 7 —TEST 27, ALLOY 571 (0 04 PER CENT C, 15 3, 0 NI)
FIG. 8 —TEST 28, ALLOY 572 (0 05 PER CENT C, 17 4 CR, 2 0 NI)
TEST 29, ALLOY 573 (0 05 PER CENT C, 17.4 CR, 4 0 NI)

showed only one negative deviation, from which it is concluded that the double point observed on heating may have been due to the preparation of the sample, or to readjustment of the dilatometer assembly.   Similar observations hold for other alloys   Consequently, in reproducing the curves for the other alloys, the first heating run has been disregarded   Heating run 3 showed only one negative deviation   Runs 2 and 4 showed an interesting change in slope at about 800° C   To see if this change in slope was reversible, heating run 5 was started before cooling run 4 reached the temperature at which a positive deviation had been observed in cooling run 2.   Surprisingly, a positive deviation, followed by a negative one, was observed   This led to the suspicion that the gamma to alpha change might take place at a higher temperature if the alloy were

very slowly cooled   Cooling run 6, in which the specimen was cooled very slowly from 800° C., demonstrated that this is the case, the positive deviation occurring over a temperature range and completed, as far as could be observed, above 400° C , which is more than 100° above the temperature at which the transformation started at the normal cooling rate. This observation was substantiated by the additional series of runs numbered consecutively from 7 to 10.

Alloy 572 (0 05 per cent C, 2 0 Ni, 17.4 Cr; test 28, Fig 8) — This alloy, containing approximately the same amount of carbon and
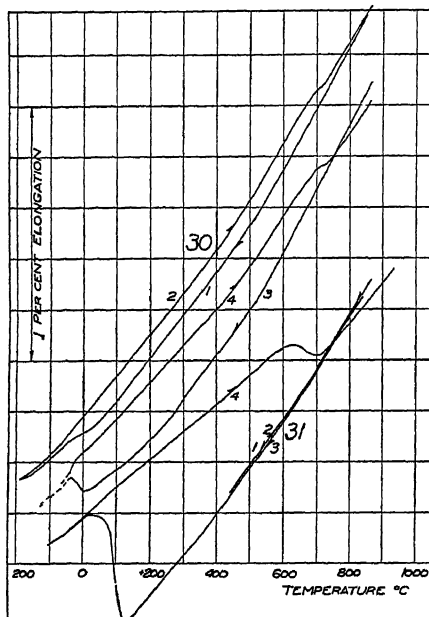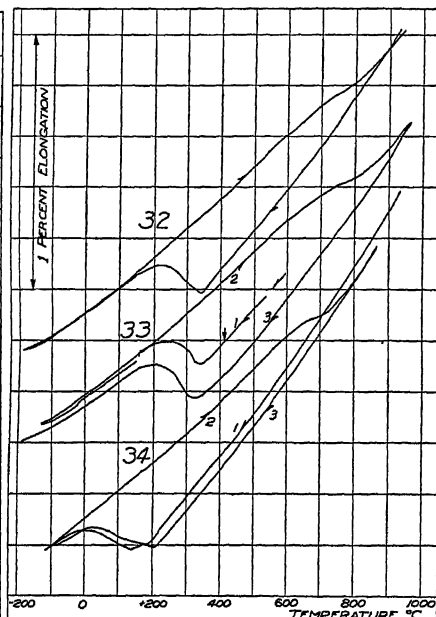
FIG. 9.   FIG. 10

FIG 9 — TEST 30, ALLOY 695 (0 16 PER CENT C, 17 7 CR, 4 2 NI).
        TEST 31, ALLOY 18-5 (0 10 PER CENT C, 17 6 CR, 5 1 NI)
FIG 10 —TEST 32, ALLOY 694 (0 20 PER CENT C, 17.3 CR, 2 1 NI)
        TEST 33, ALLOY 1-577 (0.28 PER CENT C, 18 4 CR, 2 0 NI)
        TEST 34, ALLOY 1-578 (0.25 PER CENT C, 18.7 CR, 4 2 NI).

chromium as the alloy just discussed, shows normally, as in runs 1 to 4, a pronounced positive deviation on cooling, beginning at about 200° C. and complete at room temperature, and a negative deviation on heating In an effort to start the positive deviation on cooling at a higher temperature than obtained at the normal rate, the sample was held, in run 5, at about 700° C. for 1 hr., then at about 450° C. for 42 hr.   No expansion was observed during this long soak at a temperature well below that at which the transformation occurred on heating.   The change in slope on subsequent cooling indicates that the slow rate employed effected a partial transformation.

Alloy 573 (0 05 per cent C, 4 0 Ni, 17 4 Cr, test 29, Fig 8).—The effect of the increased nickel content has been to increase the magnitude of the volume change, and to lower somewhat the temperature of the transformation on cooling

Alloy 1-574 (0 05 per cent C, 7 8 Ni, 17 2 Cr; test 35, Fig 11) —A definite transformation was found in this low-carbon 18-8 alloy on heating and cooling   The transformation on cooling occurs below room temperature and the sample must be cooled below 0° C before the transformation on heating can occur   The heating transformation occurs at over 600° C at the normal rate of heating

Alloy 18-8-01 (0 01 per cent C, 8 Ni, 18 Cr, test 36, Fig 11) —An 18-8 alloy of exceptional purity[6] containing only 0 01 per cent carbon
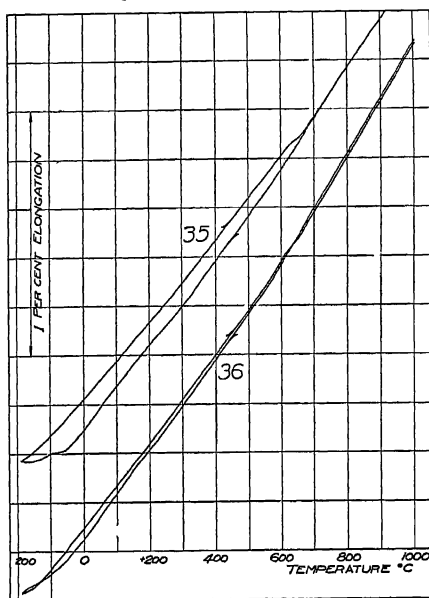
FIG 11   FIG. 12

FIG 11 —TEST 35, ALLOY 1-574 (0 05 PER CENT C, 17 2 CR, 7 8 NI).
TEST 36, ALLOY 18-8-01 (0 01 PER CENT C, 18 CR, 8 NI).
FIG. 12 —TEST 37, COMMERCIAL 18-8 (0 13 PER CENT C; MAGNETIC SUSCEPTIBILITY 230).
TEST 38, COMMERCIAL 18-8 (0 13 PER CENT C, MAGNETIC SUSCEPTIBILITY 150)
TEST 39, COMMERCIAL 18-8 (0 13 PER CENT C, MAGNETIC SUSCEPTIBILITY 330)
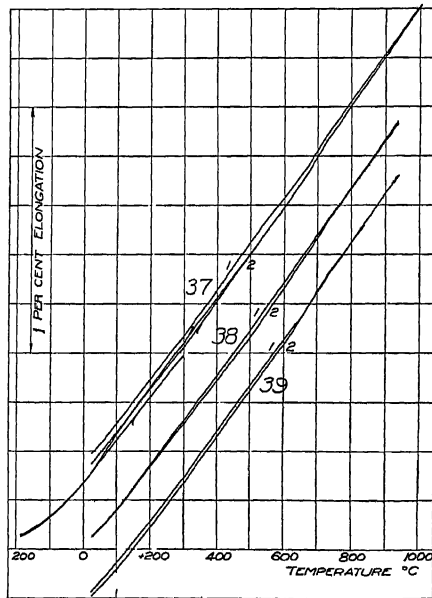
was included in this study   Some slight indication of a transformation occurring below room temperature on cooling and at over 600° C on heating was observed   (The crossing of the curves in the illustration is due to a slight displacement in the dilatometer assembly at the temperature of liquid nitrogen)   No deviation from the normal heating and

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[6] This alloy was melted under argon, using exceptionally pure electrolytic chromium, nickel and iron

cooling curves could be detected for a commercial 18-8 containing 0 13 per cent carbon (test 37, run 2, Fig 12)

Alloy 694 (0 17 per cent C, 2 2 Ni, 17 1 Cr, test 32, Fig 10) —This alloy behaves very much like that containing only 0 05 per cent carbon (test 28, Fig 8), except that the transformations occur at slightly higher temperatures   It is very different from the 0 16 per cent carbon, 4 2 per cent nickel alloy (test 30, Fig 9)

Alloy 695 (0 16 per cent C, 4 2 Ni, 17 7 Cr, test 30, Fig 9) —A comparison of this alloy with the similar one containing 0 05 per cent carbon (test 29, Fig 8) shows the influence of carbon   The magnitude of the transformations is apparently less for the higher carbon content, but it is much affected by the rate of cooling   Run 3 was made at a much slower rate of cooling than run 1, resulting in a more definite positive deviation, occurring, however, at approximately the same temperature   This alloy was held at the temperature of liquid nitrogen for 11 hr.   The subsequent heating run, No. 4, shows a greater negative deviation than the previous heating run.

Alloy 18-5 (0 10 per cent C, 5 1 Ni, 17 6 Cr, test 31, Fig 9) —This alloy cannot be compared directly with any other, the two alloys nearest in nickel content being of the following composition one 4 per cent nickel with 0.16 per cent carbon and the other 4 per cent nickel with 0 04 per cent carbon   The 5 per cent nickel alloy is of much interest, however, because of its magnitude of dilatation and its hardenability by cold treatment after quenching.   It is to be noted that the curves for this alloy closely resemble those for the 0 05 per cent carbon, 4 0 per cent nickel alloy (test 29, Fig 8)

Alloy 1-577 (0 27 per cent C, 2 0 Ni, 18.4 Cr, test 33, Fig 10) — This alloy gives dilatation curves nearly identical with the 0 17 per cent carbon, 2 0 per cent nickel alloy (test 32)   The specimen was held at slightly over 400° C. for 40 hr to see whether the transformation could be influenced   It was noted that the influence of holding was less than in the case of the 0 05 per cent carbon alloy (test 28, Fig 8)

Alloy 1-578 (0 25 per cent C, 4 2 Ni, 18 7 Cr, test 34, Fig 10) — This test differs from the one of the similar carbon but lower nickel alloy, above, in the temperature at which the transformations occur In this alloy, the transformation is not completed at room temperature at the normal cooling rate, the transformation on heating is completed at a lower temperature   Note, by comparison with tests 29, 31 and 30 (Figs 8 and 9), that the temperature of transformation on heating remains much the same, being slightly lowered by increasing carbon content.

Commercial "18-8" *Alloys* (tests 37, 38 and 39, Fig 12) —A number of the "decomposed"[7] alloys were placed in the dilatometer and the

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[7] By "decomposed" is meant the alloys that were held for a long period of time at temperatures between 1000° and 1400° F with a subsequent appearance of a magnetic phase

initial heating runs carefully observed   Because of the doubts regarding the reliability of the data obtained on first heating, too much confidence cannot be placed in the results   Test 37 was on a 0 13 per cent carbon alloy quenched from 1600° F , test 38, on a 0 22 per cent carbon alloy quenched from 2200° F , and test 39 on a 0 22 per cent carbon alloy quenched from 1800° F   All were decomposed by soaking for 100 hr at 1400° F   Their relative magnetic susceptibilities were, in the order named, 230, 150 and 330 on an arbitrary scale, as determined with the Fahy Simplex Permeameter. The alloy with a magnetic susceptibility of 150 showed no dilatometric irreversibility, the 230 value perhaps a little, and a definite though small negative deviation was observed for the alloy whose value was 330   The curves shown in Fig 12 are all, except one, heating curves, all numbered "1" were obtained by the first heating of the decomposed samples and all numbered "2" represent a subsequent heating   The difference, which is very small, indicates the extent of "decomposition " A cooling run was made in test 37 to complete the data for the commercial 18-8 alloys   No anomalous dilatation was observed, contrary to the behavior of alloys with 0 01 and 0 05 per cent carbon. Again, let it be emphasized that the magnitude of the dilatation is of the order of reproducibility obtainable with the dilatometer   Consequently, too much reliance on the observations on the decomposed alloys would be unwise

DISCUSSION OF RESULTS

Although many alloys were tested dilatometrically and for increase in hardness, there has been no opportunity to check the results by varying the composition within narrow limits   The results obtained so far are presented in graphic form in Fig 13, and will serve as an outline for a more comprehensive work, in progress, to establish the limits of composition and conditions of treatment for changing the mechanical characteristics of chromium-nickel-carbon alloys, together with a study of their corrosion resistance   The alloys that are hardenable by the treatment described lie within the area between the two dotted lines in Fig 13   The alloys lying to the left of this area cannot be retained sufficiently austenitic by quenching[3] to enable them to be hardened by being subjected to low temperatures   In those to the right of the dotted line, austenite preserved at room temperature by quenching is sufficiently stable (sluggish?) not to be decomposed by simply lowering the temperature. The question of thermodynamic stability, however, is not one to be settled by this simple method, especially when the alloys possess a lattice as distorted as these must have, since there are a large number of stranger atoms in the normal lattices of iron

[3] V. N Krivobok and M A Grossmann Influence of Nickel on the Chromium-Iron-Carbon Constitutional Diagram   *Trans* Amer Soc Steel Treat (1930) 18, 808

This investigation has established that, for a given nickel content, the amount of carbon that will produce hardening is limited to a rather narrow range, but as the nickel content decreases and carbon increases, this range becomes broader   With 8 per cent nickel, a carbon content of about 0 05 per cent is sufficient to produce some hardening, and as the nickel content is decreased, more and more carbon is necessary   The best composition and treatment for both hardness and corrosion resistance were not determined.

The extent of hardening may be studied from Fig 13, which shows the relation between hardenability in terms of Rockwell hardness and composition of the alloys studied   Black circles in this figure indicate the composition of the alloys, the figures above the circles indicate the increase in length from dilatometric tests, and the figures below the circles indicate increase in hardness
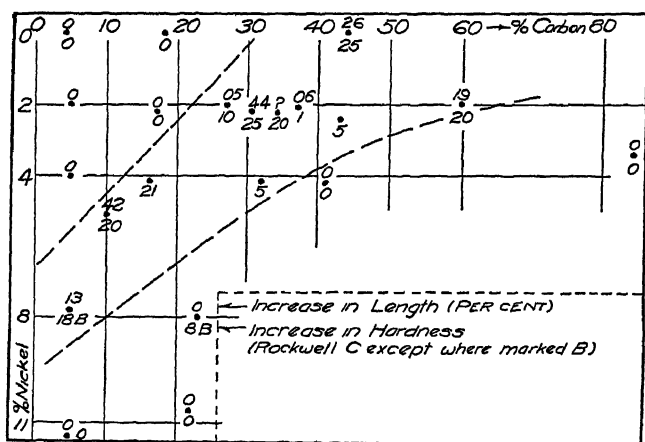
FIG 13 —SUMMARY OF TESTS ON QUENCHED ALLOYS AFTER IMMERSION IN LIQUID AIR

The results of the dilatometric runs covering the range in temperature between 1000° C (1832° F) and −190° C. (−310° F), are summarized in Fig 14, which lists the temperatures and magnitudes of the transformations on cooling

Similar data for the heating runs do not require tabulation, for the simple reason that the temperature of transformation is practically the same, approximately 600° C. (1112° F), regardless of the composition of the alloy.   It is believed that this temperature represents the eutectoid transformation and apparently nickel and carbon have little effect on the eutectoid temperature in this system   On exceeding 600° C (1112° F), the eutectoid temperature is passed and the heterogeneous field of gamma iron and either delta iron or carbides is entered.   In some cases, depending on the composition of the alloy, the temperature of 1000° C. (1832° F) is sufficiently high so that the homogeneous gamma

field has been entered, as is evidenced by a comparison of the slopes of the heating and cooling curves   Tests 28, 32 and 33 for 2 per cent nickel alloys and tests 29, 30 and 34 for 4 per cent nickel alloys show that for the former (2 per cent nickel) it is doubtful whether by heating to 1000° C (1832° F) the alloys are brought into a homogeneous gamma field   It is indicated by a relatively wide range of transformation (representing a wide heterogeneous field of alpha and gamma iron, or gamma iron and carbides)   In other words, a much broader range of temperatures is required before the heating curve assumes the characteristic slope of gamma iron   In performing cooling runs 3 and 5, test 28, Fig 8, the specimen was held at 1000° C for 40 min before starting run 5   The fact that holding at this high temperature did not change the slope of cooling run 5 as compared with the slope of cooling run 3, coupled with
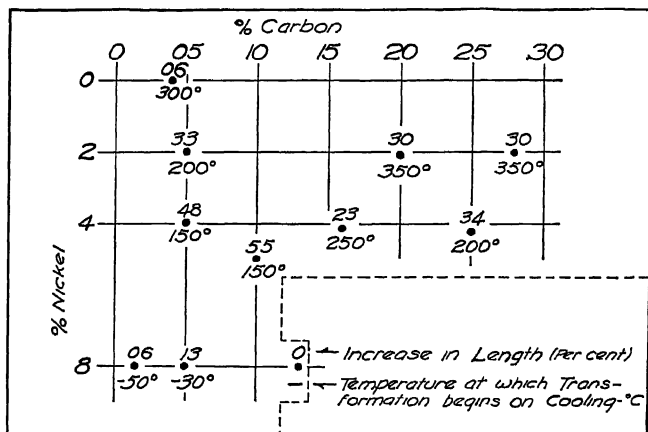
FIG 14 —SUMMARY OF DILATOMETRIC TESTS AT NORMAL RATES OF COOLING (FROM 1000° TO −190° IN ABOUT 2 HR)

the observation that heating, in run 4, very slowly from 700° to 800° C. (total time consumed being 3 hr) did not change materially the slope of the heating curve between 800° and 1000° C , is additional indication that at the temperature of 1000° C the alloys are still confined to the heterogeneous field.

It is encouraging that the data obtained from this independent dilatometric study are in good agreement with the existing constitutional diagrams

A study of Fig 14, with its information pertaining to changes on cooling, shows that the temperature of transformation depends on the carbon and nickel content. The most complete series shows the effect of nickel on alloys containing 0 05 per cent carbon   The lowering of the transformation range is gradual and on normal rates of cooling reaches −30° C in the alloy containing 18 per cent chromium and 8 per cent nickel   Remembering that no lowering was observed on heating curves,

it may be supposed that the observed lowering on cooling is due to the sluggishness (as far as the tendency to transform is concerned) brought about by the increase in nickel content   Similar observations hold true for alloys with higher carbon content

A pronounced difference in the magnitude of the transformation on heating and on cooling needs no explanation other than the difference in the coefficients of thermal expansion of the alpha and gamma phases   The magnitude of the transformation depends on the temperature at which it takes place, and on the composition, in so far as the latter affects the temperature of transformation and the coefficients of thermal expansion (for both phases, alpha and gamma)   This may account for the maximum in magnitude observed in the alloy with 4 per cent nickel   It may be well to point out, however, that a maximum in the magnitude of a dilatometric transformation does not necessarily mean a maximum in the resulting hardening effect   This is illustrated by alloy 573 (test 29, Fig 8) and No 18-5 (test 31, Fig 9), although both have about the same magnitude of dilatation, the hardness of the 18-5 is increased about 20 points on the Rockwell C scale, while alloy 573 has an increase of less than 10 points   Apparently the increase in hardness on cold treatment depends on the same conditions that are recognized in the process of quenching, such as the original grain size of the austenite, quantity of austenite retained by quenching, size and distribution of the hardening phase, etc

The dilatometric curves for these same two alloys are practically identical, despite a difference in composition.   A similar observation can be made by comparing test 28, Fig 8, and test 34, Fig 10, for alloys containing respectively 0 05 per cent carbon, 2 0 per cent nickel and 0 25 per cent carbon, 4 2 per cent nickel, although in the latter the transformation is spread over a wider temperature range   Whether this similarity in dilation curves indicates the opposing effects of carbon and nickel is a question requiring additional data, although the facts that increasing carbon content raises the temperature of transformation in both the 2 per cent and the 4 per cent nickel series, and that increasing the nickel content lowers the temperature in the 0 05 per cent, 0 16 to 0 20 per cent, and 0 25 to 0 28 per cent carbon series are strong confirmatory evidence.

This discussion applies to the normal rates of heating and cooling, as defined on page 8 of this paper   It may be supposed that slower rates of heating or cooling would considerably affect the temperature at which the transformation occurs, and that as a consequence, by holding the sample below the hypothetical equilibrium temperature and above that at which the transformation is observed to occur at the normal rate, the transformation temperature may be raised.   The holding experiments described in the section on Experimental Results clearly

indicate that the raising of the transformation temperature can be accomplished in the alloy containing 0 04 per cent carbon and no nickel, that when the nickel is increased to 2 0 per cent, the phenomenon is less pronounced; and that when the alloy contains 0 27 per cent carbon and 2 0 per cent nickel, the effect is absent   This observation leads one to believe that both nickel and carbon make the alloys less sensitive to the holding treatment   That the phenomenon of shifting the temperature of transformation cannot be accounted for by considering the homogenizing effect of the prolonged heating is illustrated by runs 7 and 8, test 27, Fig 7   These runs were obtained at the normal rate of cooling of the specimen that previously was made to transform at a higher temperature by the holding treatment described

An experiment was carried out to ascertain the effect of the rate of cooling on the progress of the decomposition of austenite, retained at room temperature by quenching and subsequently subjected to cold treatment   It was found that cooling to a temperature below that at which the transformation had begun and holding at that temperature would not cause the transformation to proceed to completion   Completion necessitates further lowering of the temperature, as may be seen from test 26, Fig 6

This experiment points out that for a given temperature just so much of the retained phase will be decomposed   In other words, the alloy may be considered to exhibit a quasi-equilibrium between a stable and a metastable phase, similar to the condition observed in the iron-carbon system and described by Hannemann [9]

In connection with the studies of the effect of the rate of cooling, an observation very pertinent to the subject under discussion may be described   Previous studies of an 18-8 alloy very low in carbon (the exact carbon being 0 01 per cent) have shown that this alloy readily separates a magnetic ferritic phase, not only detectable by magnetic measurements but clearly observable under the microscope, presenting, as it were, a Widmannstatten structure   This magnetic phase, however, necessitated, for its appearance, a holding at almost any temperature above 260° C (500° F)   From a study of the slopes of the dilatometric curves one can judge whether a certain curve represents the dilatation of either the gamma or the alpha phase   Test 36, Fig 11, gives the curve for this 18-8 alloy with 0 01 per cent carbon.   The slope of this curve is typical of chromium-nickel austenite, and since the presence of even small amounts of the alpha phase would result in deviations from the normal slope, it is to be concluded that at the normal rate of cooling apparently no alpha phase is separated until the alloy is cooled to a temperature below 0° C (−32° F).

[9] H Hanemann and A Schrader On Martensite *Trans* Amer Soc Steel Treat (1926) **9**, 169.

The changes taking place when commercial 18-8 alloys are held for long periods within the temperature range of 1000° to 1400° F are fairly well known. These changes have been referred to as "decomposition" of the austenitic 18-8 steel, resulting in the formation of a relatively small amount of a new constituent, presumably carbides, while it is believed that through the impoverishment of the matrix with respect to chromium, and possibly nickel, some alpha solid solution is also formed [10] The most sensitive test yet applied to the detection of the decomposition and its extent is the determination of the alloys' relative magnetic susceptibility, which may be due either to alpha iron or carbides Since the magnetic susceptibility of alpha iron is known to be much greater than that of carbides, if the increase in magnetism of the alloy were due to the magnetism of carbides (and not to the alpha solid solution), a considerable dilatation, on heating of the alloy, should be expected, because of the relatively large amount of carbides necessary to produce any considerable magnetism

Consequently, the dilatometric runs on decomposed samples of 18-8, as described on page 339, were made for the purpose of confirming by dilatometric evidence the presence of alpha magnetic iron in decomposed chromium-nickel alloys (in this particular case, of 18 per cent chromium and 8 per cent nickel composition) The small dilatometric irreversibility observed for the alloys which were perceptibly magnetic after decomposition is considered to be good evidence of magnetic alpha iron

SUMMARY

Certain chromium and chromium-nickel steels in the stainless range can be hardened by a treatment consisting of a rapid cooling to room temperature followed by immersion into a liquid well below room temperature A mixture of solid carbon dioxide and acetone provides a sufficiently low temperature to accomplish this increase in hardness, which in several alloys has resulted in hardness of over 50 Rockwell C.

The study of the process of hardening was made, using for this purpose dilatometric observations It has been demonstrated that the increase in hardness is due to the decomposition of austenite at low temperatures and that the progress of the phase change is a function of temperature Only a few minutes are necessary to establish a quasi-equilibrium between the retained, metastable austenite and the chromium-nickel ferrite and carbides, at any temperature.

The effect of nickel on iron and chromium alloys containing about 18 per cent chromium is to lower the temperature at which the gamma to alpha transformation occurs on cooling, and to oppose raising this

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[10] Except in 18-8 alloy very low in carbon in which magnetic alpha ferrite separates directly from austenitic solid solution

temperature by "soaking," as can be accomplished in iron and chromium alloys containing little or no nickel. The effect of carbon is the same in this latter respect, but its effects on the temperature of transformation on cooling is less than that of nickel   With 0 05 per cent carbon between 4 and 8 per cent nickel is necessary to retain some of the austenite on quenching, but as the carbon content is increased to about 0 25 per cent, 2 per cent nickel is sufficient.

It is believed that the treatment as described may, and probably does, considerably change the mechanical properties of chromium-nickel-iron alloys   The necessity for further investigations is stressed and the tentative plans for immediate future work indicated

DISCUSSION

(F N. Speller presiding)

O V GREENE, West Reading, Pa (written discussion) —Since only a narrow range of chromium-nickel alloys is included in our work, this discussion will be confined to alloy 18-5   The curves of tests 16 and 17, Fig 4, agree with our temperature-permeability curve on a similar alloy   In spite of the fact that the data in each instance were obtained by vastly different methods, both curves show that the transformation of the retained austenite starts at about 0° C and continues over a range to about −60° C   It is assumed that the specimens used for tests 16 and 17 were quenched before dilatometric determinations were made   Incidentally, it is also possible to show the start of this transformation thermally by means of a bismuth-tellurium couple   However, if tests are re-run without again quenching from about 2000° F , no thermal, magnetic or dilatometric change will be found in this low-temperature range   This is shown in test 18 of Fig 4, which evidently represents a second run with one of the previously cooled specimens   No dilation was observed, for all of the retained austenite had been converted to martensite during the first cooling

If the dilatometer curve of test 31, Fig 9, is compared with those of tests 16 and 17, Fig 4, it will be seen that in the latter the dilation at the point we have chosen to call Ar″ has been depressed about 100° C   We believe this alloy is too sluggish to permit the Ar′ transformation   The critical cooling rate of this alloy is such that austenite will not be retained unless it is quenched   When cooled slowly, as in the cycle of test 31, the austenite is probably partly converted to martensite before room temperature is reached   Further change is so gradual that it cannot be detected

If austenite is retained in the specimen by quenching, the transformation observed at about 110° C will be depressed to approximately 0° C However, it should be noted that the hardness obtained by cooling quenched specimens to below room temperature is considerably greater than that obtained when specimens are cooled slowly from a higher temperature to room temperature For example, this alloy has the following characteristics

	Brinell Number	Bmax H-300	Specific Volume
As rolled	293	2700	0 127310
As quenched from 2000° F , and cold-treated to −112° F	444	9240	0 129171

The temperature of the upper transformation which occurs at approximately 600° C has been called the eutectoid transformation in this paper Our data in regard to this point were obtained by magnetic methods In our work this upper critical appears to be an A_2 point since changes in the slopes of our magnetic curves were observed at approximately the same temperature both on heating and cooling This point is always found irrespective of previous history

Low-carbon Steel

By H B Pulsifer,* Cleveland, Ohio

One of the most common basic open-hearth furnace products is a simple carbon steel with a carbon range from 0 05 to 0 15 per cent   The material is widely used for sheets, tubes, bars, wire and the innumerable special objects of secondary fabrication   The properties of the material vary over wide ranges, depending on the more exact composition and details of manufactuie or treatment that affect its structure

The present paper is a review of those properties and structures that have been found by studying this steel as used in the cap screw industry At first glance this might be thought a narrow application of the steel, but, since the industry uses the material in the cold-worked, annealed and heat-treated conditions, the title of the paper may be excused for its comprehensiveness   Yet, in studying the wide ranges of properties and structures that preclude a more specific title, there can be no suggestion of completeness or finality   Even a summary of a few years' work is no more than a preliminary survey of a field that will be fertile in scientific data and industrial products for many years to come

An outline of the structures will be given first, then a list of the previous contributions that are at hand and finally some details of the work and related problems, especially concerning this low-caibon steel in the surface-hardened condition

Wire Used in Manufacture of Cap Screws

The wire that is used for making cold-upset and roll-threaded cap screws has been cold-drawn from hot-rolled rods that were pickled and limed   The common sizes used in the industry range from 0 185 to 0 750 in dia , the exact diameters depending on the plant practice and having the usual tolerances of 0 002 in for the smaller sizes and 0 003 in for the larger sizes   The carbon range, by pit analysis, is usually between 0 07 and 0 12 per cent   Manganese should be within the usual 0 30 to 0 50 per cent range   Sulfur rarely exceeds 0 045 per cent. and phosphorus seldom exceeds 0 030 per cent   Silicon is usually below 0 03 per cent but in the silicon-killed steels may be in the customary 0 10 to 0 25 per cent range   Rimmed steel is not considered most suitable for cap screws that are cold-headed or for parts that are to be surface-hardened

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This steel is eminently suitable for ordinary cap screws   Only when testing for precise properties or in etching or microscopic study is it found to be afflicted with the irregularities inherent in the making of steel and the fabrication of commercial wire   Hot rolling, pickling and cold drawing may leave their marks that are superimposed upon changing and irregular carbon content, decarbonized exterior, laminations, segre-
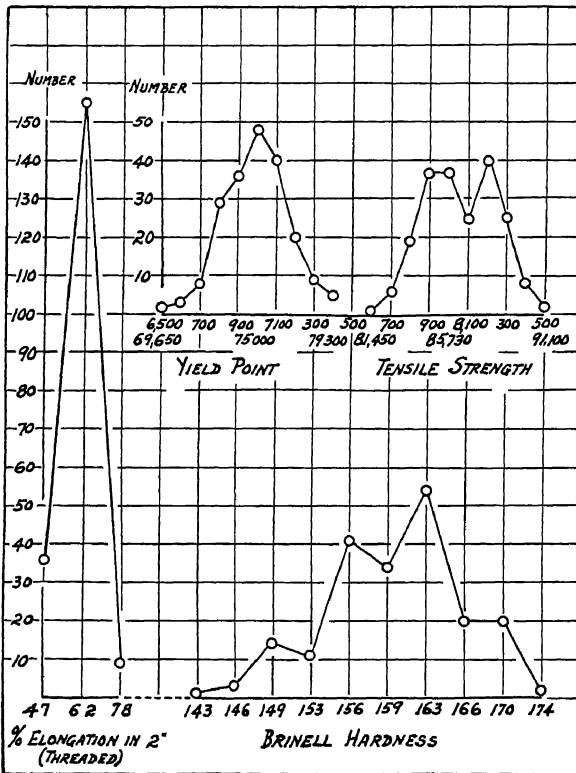
FIG 1 —DISTRIBUTION CURVES OF PROPERTIES OF 200 CAP SCREWS
Screws were 7/16 by 2½ in with coarse threads, cold-headed and roll-threaded
They had no heat treatment   Carbon = 0 10 per cent

gated cores, slag and refractory inclusions, elongated blowholes and pipe residuals   Pit analyses and average properties are one thing, inch by inch compositions and properties are an entirely different matter.

The physical properties that may be expected in this type of cold-drawn wire as used for cap screws are typically represented by the figures of Table 1.   These are the average of three tests on the wire used for making the cap screws that were tested for Fig 1   Similar figures are given for the average values of three lengths after annealing in a tube at 1700° F

TABLE 1 —*Properties of Low-carbon Wire*

Carbon = 0 10 Per Cent

	Cold-drawn Wire	Annealed Wire
Actual diameter of wire, in	0 424	0 424
Scleroscope hardness[a]	30–35	17–18
Brinell hardness[b]	126	80
Elastic limit (dividers), lb per sq in	42,800	28,800
Yield point (drop of beam), lb per sq in	52,710	28,800
Tensile strength, lb per sq in	70,210	54,600
Fracture load, lb per sq in	120,200	122,500
Reduction of area, per cent	61 7	71 6
Elongation in 10 in , per cent	5 0	34 0
Elongation in 2 in , per cent	17 7	50 0

[a] Scleroscope hardness of the cold-drawn wire is determined on the coated surface, the annealed wire is tested on a filed surface

[b] Brinell hardness of the cold-drawn wire is made with 3000-kg load, the annealed wire flattens under this load, so only 500 kg is used for that

The simplest way of making cap screws from this wire is to cold-upset the heads and simultaneously shrink the section to be threaded to the pitch diameter ready for roll threading   Pointing, trimming the hexagon on the head, and roll threading complete the essential operations in manufacturing the cap screw   An etched longitudinal section through a $\frac{7}{16}$ by 2½-in coarse-threaded cap screw made from cold-drawn wire is shown in Fig 2   The shaded cross in the center of the head indicates the zone of greatest plastic flow during the cold heading operation   The threads have also had varying amounts of cold deformation that is not conspicuous on this small print

When a lot of these cap screws is made from a coil of wire they are cut off and put through the machinery in the most unvarying manner, so that their physical dimensions differ by only a fraction of a thousandth of an inch, yet it is surprising that their physical properties spread over a considerable range   It is freely admitted that small deviations arise from physical dimensions, inequalities in the successive testings, and from personal and observational errors   These deviations, however, are of a smaller order of magnitude than those based on changing composition, varying structural make-up and inequality of metal flow The three latter irregularities begin in the steel ingot and, continuing through billet and hot-rod stages, are not difficult to find in the cold-drawn wire   Finally intensified in the cold-formed cap screws, the results are strikingly and systematically diversified

To demonstrate the spread in properties of similar cap screws made in sequence from a single coil of cold-drawn wire, 200 of the $\frac{7}{16}$ by 2½-in. cap screws were tested for hardness on the top of the center of the head

and then pulled in the tensile machine. The results are plotted in Fig. 1. They show that the hardness of the upset heads ranged from Brinell 143 to 174 with a most frequent value of 163; the yield points ranged from 69,650 to 79,300 lb. per sq. in. with a most frequent value of 75,000 lb. per sq. in.; the tensile strengths ranged from 81,450 to 91,100 lb. per sq. in., with a mean value of about 85,730 lb. per sq. in., and the elongations ranged from 4.7 to 7.8 per cent. in 2 in., with a most frequent value of 6.2 per cent.

These distribution curves have more than casual meaning. From them we gain a picture of the inequalities that exist in supposedly "uniform" pieces. Other studies[1] demonstrate that threaded sections give wider variations than standard straight test-bar sections; the strengthening effect of the threads also increases the yield point and tensile strength. But in spite of these handicaps the cap screws render a great service in making numerous tests possible. They may be considered as extremely convenient although modified test specimens. Further, in testing for small induced variations, as by low-temperature annealings, we shall become suspicious of apparent changes of which the values come within the "spreads" of the pieces already tested. We shall at least require a consistent trend in results before a definite alteration is accepted. Further, these results, as well as other distribution curves,[2] disclose the fallacy of attempting to state an exact quantity for the properties of any particular composition of steel, or for any particular treatment of a steel. Accordingly, we are discreet if we use the mean of several tests and express results as within a range instead of by one challenging figure.

FIG. 2.—ETCHED LONGITUDINAL SECTION THROUGH CAP SCREW.

Screw was ⁷⁄₁₆ by 2½ in. —14. Cold-upset and roll-threaded from 0.424-in. wire. Shaded cross in head indicates zone of greatest grain distortion and change of "fiber" direction.

CHANGES IN STRUCTURE CAUSED BY HEATING AND QUENCHING

It is necessary to describe the structure of the cap screw shown in Fig. 2 and explain the changes that take place on heating and quenching. Further investigations doubtless will add to this rather lengthy account.

[1] H. B. Pulsifer: The Physical Properties of Fine Bolts. *Trans.* Amer. Soc. Steel Treat. (1930) **18**, 273.

[2] H. B. Pulsifer: *Loc. cit.*

E. J. Janitzky: Correlating Test Data on Heat-treated Chromium-vanadium Steels. *Jnl.* Soc. Automotive Engrs. (1928) **22**, 55.

This cap screw was made by cutting off a piece of cold-drawn wire that had received some 18 per cent reduction in the drawing   In heading the cap-screw blank, the metal received a varying cold deformation amounting to probably 85 per cent reduction in the center of the flowed zone The entire stem was slightly deformed in the upsetting, but the threaded end received far more deformation during the extrusion and subsequent roll threading

When a piece of this sort is gradually heated the first important change is the recrystallization of the most severely worked zones   This begins at approximately 1000° F when heated for 20 min   It has not been possible to be sure of changes at lower heats and we are not especially interested in the recrystallization of the threads

On continued heating the newly formed grains in the head increase in size with the small patches of pearlite still in their original condition But, with the temperature reaching some 1300° F , the pearlite changes to gamma solid solution, or homogenizes   This is a very important event for, upon sharply quenching after this happens, martensitic nodules can be obtained in place of the original pearlitic masses   As a matter of fact, all sorts of conditions may be found   areas that are partly pearlitic and partly martensitic, all martensite, or martensitic kernels with troostitic or sorbitic fringes, or troostitic kernels with sorbitic fringes

When the temperature is increased above this homogenizing of the pearlite, the carbon begins its diffusion into the surrounding ferrite and its strained grains begin their germinative growth. As the carbon diffuses it forms the more and more dilute gamma solid solution while the alpha matrix is absorbed in the new phase   Both the diffusion and grain growth end only at and above the upper critical temperature of some 1650° F.   Pieces quenched from 1325° to 1650° F display a great variety of structures, depending on the original carbon content, the amount of previous strain, the temperature, the time of soaking and the rapidity of the quenching.

If a piece of the steel is heated above its upper critical temperature its carbon should be uniformly dispersed and the structures that are found after quenching will depend on the rapidity of that quenching   Quenchings into slowly moving water or oil are slow enough to allow troostitic or sorbitic lamellae to form in the ferrite and the steel is not brittle   But quenching into a rapid stream of cold water or pumped caustic solution that makes a continuous forced contact of coolant and metal will give mixtures of martensite and ferrite, or practically pure martensite   Increasing the carbon from 0 10 to 0 16 per cent greatly assists the formation of martensite

This outline of what happens during the heating and quenching of low-carbon steel is further explained by Tables 2 and 3 and by the photomicrographs (Figs 3 to 10).
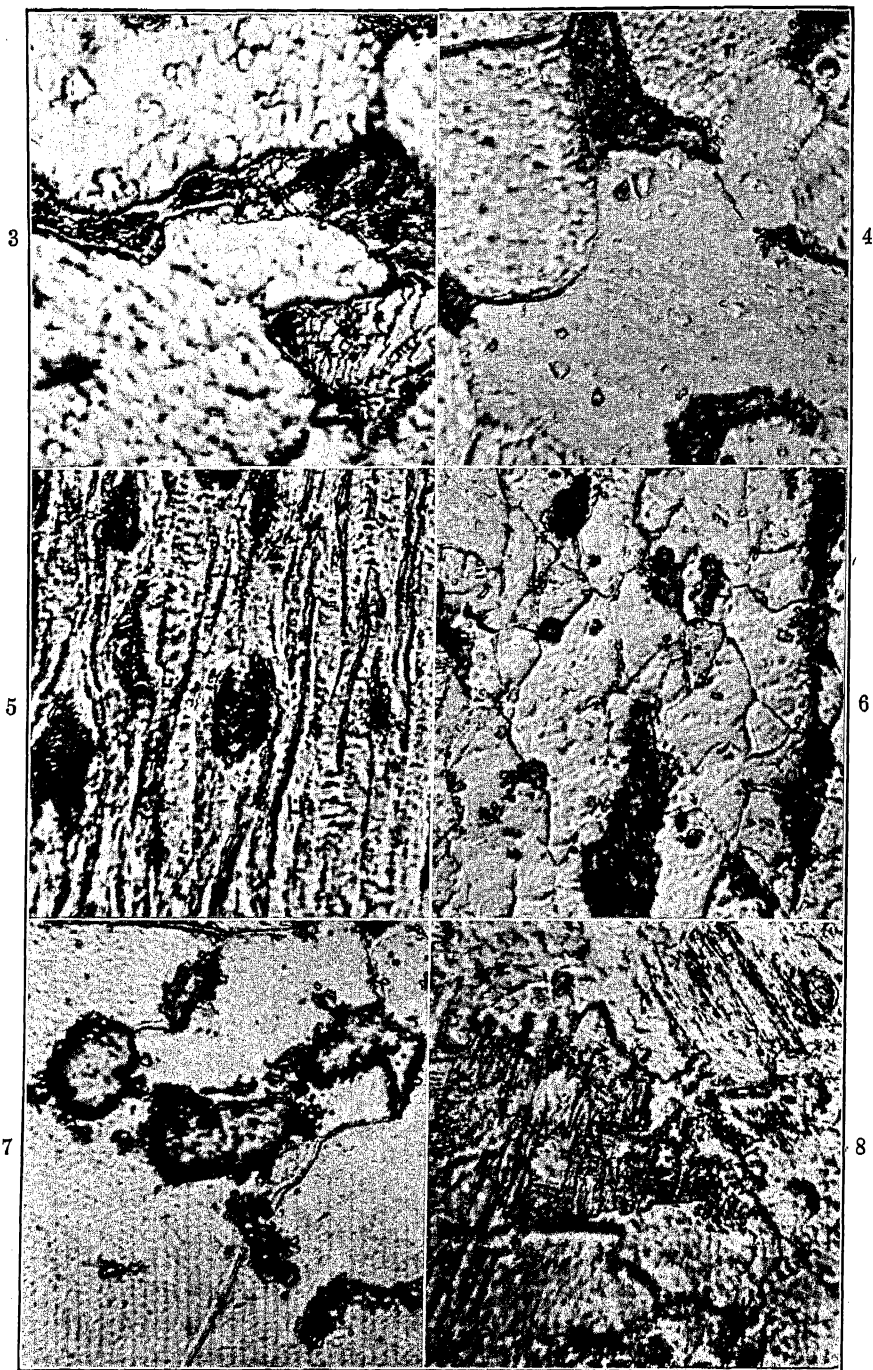
TABLE 2 —*Structural Changes in Low-carbon Steel*

	On Heating	On Cooling		
Deg F		Forced Quench	Water Quench	Deg F
1800		Martensite	Dispersed troostite	1800
1700				1700
1600	Alpha ferrite ab-sorbed	Martensite and fer-rite		1600
1500	Ferrite grains grow	Martensitic span-gles	Troostitic spangles	1500
1400	Carbide diffuses			1400
1300	Pearlite homoge-nizes	Martensitic nodules	Troostitic nodules	1300
		Original pearlite		
1200				1200
1100	Deformed ferrite re-crystallizes	Deformed ferrite recrystallized		1100
1000				1000
	No change	No change		

To illustrate the structures that determine the properties given in Table 3 we may start with a cap screw that has been heated to 1700° F , or over, and slowly cooled in the furnace   A longitudinal section through the stem of such a piece is given in Fig 3 at 1000 dia   This shows merely large masses of pearlite between large grains of ferrite   Both pearlitic masses and ferrite grains are much larger than in the original wire, and although the pearlite seriously inhibits the free growth of the ferrite grains, low magnifications disclose a decided tendency for the ferrite grains to shape accordingly to a tetrakaidecahedral motif   The

FIG 3 —LONGITUDINAL SECTION OF FULLY ANNEALED CAP SCREW   × 1000
Large masses of pearlite in large ferrite grains   Properties given in Table 3, column 1
FIG 4 —LONGITUDINAL SECTION OF COLD-FORMED CAP SCREW OR ORIGINAL WIRE
× 1000
Normal sizes of ferrite and pearlite units   Properties given in Table 1, column 1
Properties for this material after strengthening by rolling threads, Table 3, column 2
FIG 5 —LONGITUDINAL SECTION THROUGH CENTER OF UPSET HEAD OF CAP SCREW
× 1000
Ferrite grains elongated at right angles to trend in Fig 4   Brinell hardness about 207.
FIG 6 —CENTER OF RECRYSTALLIZED HEAD, LONGITUDINAL   × 1000
When this stage is reached, hardness of head may be only Brinell 126 yet yield and tensile of cap screw have decreased only slightly
FIG 7 —NODULES WITH MARTENSITE CORES IN CAP SCREW QUENCHED FROM JUST
ABOVE 1300° F   × 1000
This type of structure gives brittleness, either strong and brittle or weak and brittle, depending on details
FIG 8 —DISPERSED TROOSTITE STRUCTURE OBTAINED BY QUENCHING CAP SCREWS IN
WATER FROM 1700° F   × 1000
Matrix clearly ferrite interspersed with lamellae of carbon-rich segregate

softness, weakness and ductility of the material are at their maxima in this condition.

Fig. 4 is a print of the cold-formed cap screw at 1000 dia. as taken longitudinally in the stem. This is sensibly the structure of the original wire with grains of ferrite of normal size and small masses of pearlite more or less uniformly distributed.

TABLE 3.—*Properties of $7/16$ by $2\frac{1}{2}$-In. -14 Cap Screws*
Carbon $= 0.10$ Per Cent.

	Fully Annealed	Cold Formed	Nodular	Dispersed Troostite	Ferrite and Martensite	Martensite
Brinell hardness.........	80	163	174	146	212	255
Yield point, lb. per sq. in.	29,000	75,000	80,000	66,000	109,000	135,000
Tensile, lb. per sq. in....	52,000	86,000	105,000	90,000	120,000	150,000
Elongation, in 2 in., per cent. (threaded)....	15.6	6.2	6.2	8.0	1.5	1.0
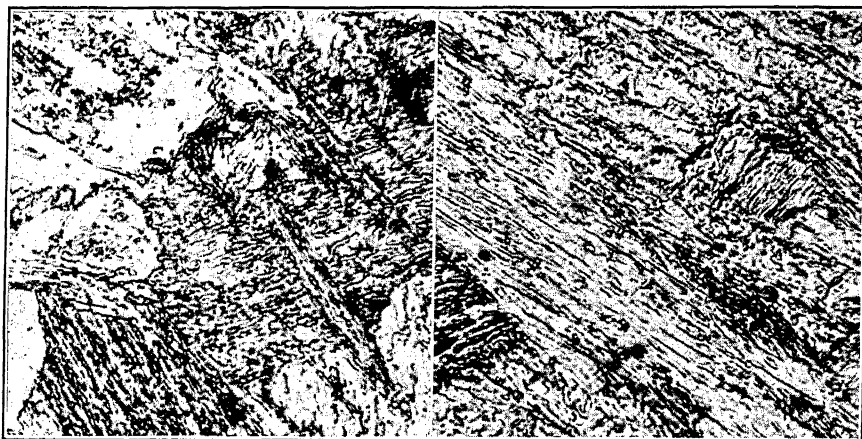
FIG. 9.—SECTION OF 0.10 PER CENT. CARBON CAP SCREW QUENCHED TO GIVE MARTENSITE AND FERRITE. × 1000.
Portion of ferritic network surrounding areas of martensite.

FIG. 10.—MASSIVE MARTENSITE IN 0.10 PER CENT. CARBON CAP SCREWS GIVEN FORCED QUENCH IN COLD CAUSTIC. × 1000.
Ferritic networks also are found in the specimen.

An idea of the heavy deformation in the center of the upset head is gained from Fig. 5, where the grain elongation is at right angles to that of Fig. 4. This corresponds to the center of the shaded cross in the head of the cap screw of Fig. 2. Although the Brinell hardness taken on the top of the head is only 163, if the head is filed away to the center the hardness will be found about 207. The scleroscope hardness is about 40. This is still somewhat short of the Brinell 255 and sclero-

scope 65, which are found when the metal is still further deformed by other methods

This means that the cap screw, as a whole, will endure more deformation, either in service or by destructive testing, without fracturing   In normal use the cap screw fails in the threaded section and the head does not reach a critical test

At the temperature of recrystallization, some 1000° F , or slightly higher, the deformed ferrite of Fig 5 transforms to the equiaxed grains of Fig 6, which shows the unaltered areas of pearlite   Many interesting and peculiar steps can be found in this recrystallization, which begins at certain centers and spreads through mixed zones of old and new material until the entire matrix has the new characteristics   The main section of the cap screw apparently is only slightly altered by this first recrystallization in the head, the gross yield point and tensile strength remain the same   But with a little higher heating, noticeably at 1100° F , much of the stiffness caused by the cold working is lost and the properties rapidly lapse toward those of the fully annealed condition

Sharp quenching of the cap screws from slightly above the temperature of homogenization of the pearlite causes the formation of the martensitic nodules, one variety of which is seen in Fig 7   In this print the nodules are surrounded by fringes of troostite or sorbite and are not sensibly larger than the original pearlitic areas   It is common to find the nodules entirely martensitic near the outside of a specimen, farther in they may have only martensitic cores and near the center they may be mixed troostite and sorbite, or sorbitic   Indeed, pearlite itself is not infrequently a component of the nodules, especially of those formed at the lowest possible temperature and of the highly sorbitic ones

The nodular condition is naturally undesirable for toughness and ductility, for the elongation given in the third column of Table 3 is an average but far from uniform quantity, all of the properties of the steel when in this condition are subject to wide variation

Let us now pass to the structures that are found on quenching from still higher temperatures   As the degree of heat increases the carbon diffuses more and more, what is to be found in the cooled steel will depend on the *rate* of cooling   A quick quench will catch the solid solution more or less rigidified, while slower cooling will allow the coalescence of both ferrite and the eutectoid segregate   Many fantastic structures result from intermediate rates of cooling, spiked rosettes, spangles and strings of reticulated troostite may be found   A very common pattern retained by a water quenching from above the upper critical is the one that may be called that of dispersed troostite

One of these dispersions is seen in Fig 8, its properties are given in the fourth column of Table 3   The carbide segregate appears in parallel lines related to the antedecent solid solution, as well as partly defined

by the curved boundaries of the coalescing ferrite Since the ferrite phase is practically continuous, with the harder phase thinly dispersed, we find a fairly soft and ductile material This general structure is easily and consistently obtained, but its low yield point gives it secondary importance over the cold-formed pieces for engineering purposes Strength and ductility have been won at the expense of stiffness

Simple water quenching of a 0 10 per cent carbon steel does not produce appreciable amounts of martensite in objects like commercial cap screws and from temperatures practicable for ordinary plant practice But some martensite can be won if the water is forcibly sprayed or pumped upon the hot pieces With the higher ranges of temperature and with this forcing of the quenching, especially with the use of a cold 5 per cent caustic solution, more and more martensite can be won even in a steel with carbon as low as 0 10 per cent A structure largely martensitic is shown in Fig 9, while typical properties are given in the fifth column of Table 3 The steel is brittle The ductility is low and the yield point is gaining on the tensile strength while the hardness is above the range ordinarily considered possible for a steel of this carbon content

A wholly martensitic structure is hardly attained, according to the experiments of the author, by quenching into cold pumped caustic from 2200° F The nearest that has been obtained on the $\frac{7}{16}$-in cap screws gave physical properties recorded in the last column of Table 3 The hardness is up to Brinell 255, yield point is 135,000 lb per sq in and tensile strength 150,000 lb per sq in The ductility is very low and the pieces are brittle and snappy There appears to be no commercial use for such material A field of the massive martensite is given in Fig 10 Not far from this spot were parts of the ferritic network

With increasing carbon content the martensitic condition is more and more easily retained With 0 16 per cent carbon and quenching into cold water moderately agitated, mixtures of martensite and ferrite and a Brinell hardness of 321 are obtained A forced quench of this 0 16 per cent carbon steel raises the Brinell hardness to 332, while if the steel contains 0 35 per cent. carbon the hardness increases to Brinell 600 in the forced caustic quench

BRITTLENESS IN LOW-CARBON STEELS

In summarizing the properties of the several structures, it is evident that tough and brittle conditions alternate The pearlitic areas that are present in the softer conditions do not impart noteworthy brittleness even after considerable cold deformation, but when the pearlite is transformed into martensite or troostite nodules, the stock at once acquires undesirable properties Grain growth of the ferrite probably intensifies the undesirable properties and the metal may be relatively hard and brittle or soft and brittle

Dispersing the carbon beyond any sort of nodular stage to the more uniform condition of dispersed troostite again gives a tough and ductile material But if the solid solution is prevented from coagulating to visible troostite and a low-carbon martensite is retained, brittleness again appears This reaches its climax in a fully martensitic matrix

Altogether, this gives a picture of the low-carbon steels entirely different from that presented in even the most recent textbooks It may be found under good "authority" that steel containing less than 0 15 per cent carbon can be quenched in water without appreciable hardening or loss of ductility One authority apparently quotes another without experimental verification

The cap screw industry now uses great quantities of low-carbon and medium-carbon steels that have good strength and ductility Besides the 0 07 to 0 12 per cent material considered in this paper, other popular carbon ranges are from 0 14 to 0 20 per cent , 0 27 to 0 35 per cent , 0 30 to 0 37 per cent and more recently 0 35 to 0 42 per cent The latter range is easily susceptible of full hardening and tempering to supply parts that have good ductility with strength around 135,000 lb per square inch

PREVIOUS CONTRIBUTIONS

In reviewing some of the available contributions relating to the structures and properties of the low-carbon steels, there may be mentioned first the comments made by Hillman[3] in 1922 He states that the lowest temperature for practical annealing of cold-upset stock is 1150° F. and that heating into the range 1280° to 1380° F causes coarse crystallization He recommends the temperature range 1650° to 1675° F as suitable for full annealing. The statements obviously are first approximations

In 1924 and 1925 Smith[4] reported on the properties and structures of low-carbon steel that was given a drastic water-spray quench No reason was given for the brittleness found on quenching from 1300° to 1500° F. The maximum tensile strength found for pressure quenching a 0 09 per cent carbon steel is given as 122,000 lb per sq in He states that with 0 09 to 0 15 per cent carbon in the steel a maximum of 160,000 lb per sq in tensile strength can be obtained Photomicrographs of the low-carbon martensite at 500 dia are reproduced His discovery of the low-carbon martensite is important but otherwise the report is sketchy and incomplete

United States patent number 1592181, filed in 1925 by W J Crook and issued in 1926, is an interesting document Its first claim reads as

[3] V E Hillman Cold Headed Bolts—Their Metallography and Heat Treatment *Trans* Amer Soc Steel Treat (1922) **2**, 369

[4] R H Smith High Tensile Strengths with Low-Carbon Steel *Proc* Amer Soc Test Mats (1924) **24**, 618

Some Physical Properties of Low-Carbon Steel *Trans* Amer Soc Steel Treat (1925) **7**, 569

follows "1 A plain carbon steel of high elastic limit and sufficient ductility for structural and similar purposes as herein mentioned, in martensite and ferrite form and containing not over 0 25 per cent carbon and between 0 5 per cent and 1 per cent manganese " In the second claim the presence of iron carbide in beta iron is patented, which is a most sensible warning that beta iron should be commercialized with restrictions

The commercial application of the Smith process of spray quenching was described in papers by Shaner[5] and Ross[6] without further scientific data   And finally, attributed to changing industrial conditions, the abandonment of the process was announced by Allen [7]

The brittleness sometimes found in cyanided low-carbon steel was discussed by Hillman and Clark[8] in 1926, who reported that low-carbon steel quenched in water from 1500° F is only slightly changed in properties but that if first cyanided the usual tests show brittleness   The cause of the brittleness is assigned to the brittle case and oil quenching is recommended. Their studies did not penetrate to the intimate details of the conditions and since oil-quenched case is not file hard their remedy is not generally applicable

The transformation of pearlite to martensitic nodules in the water-quenching of low-carbon steel seems to have been mentioned first by the author [9]   The presence of the hard nodules between the ferrite grains was considered a general cause of brittleness and it was shown that further carbon dispersion by higher heating before quenching gave ductile material

In 1928 Rockwell[10] gave a general discussion of the phenomenon of brittleness in carburized parts   Matters like the temperature of testing, depth of case, hardness of case, tempering and suddenness of blow are mentioned as affecting the brittleness   Although two photomicrographs were given, the paper is mainly concerned with the external features as affecting the brittleness

Bolsover[11] presented a paper in 1929 in which he describes brittleness induced in low-carbon steel by heating to comparatively low temperatures

[5] E L Shaner Drastic Quenching Imparts Surprising Properties to Bolts and Rivets   *Iron Tr Rev* (1925) **76**, 871

[6] E F Ross Low-Carbon Bolts Show Uniformly High Strength   *Iron Tr Rev* (1927) **81**, 1025

[7] A H Allen Improved Equipment Facilitates Heat Treatment of Bolts   *Steel* (February 26, 1931) **88**, 31

[8] V E Hillman and E D Clark Cyanide Brittleness   *Trans* Amer Soc Steel Treat (1926) **10**, 954

[9] H B Pulsifer Smoothing and Etching Cupronickel, Bronze, Brass and Steel *Trans* A I M E , Inst Metals Div (1929) 291

[10] S P Rockwell Causes of Brittleness in Carburized Parts   *Heat Treating and Forging* (1928) **14**, 1026.

[11] G R Bolsover Brittleness in Mild Steel   *Jnl* Iron and Steel Inst (1929) **119**, 473   Abstract in *Heat Treating and Forging* (1929) **15**, 714

(galvanizing) after moderate deformation   Physical tests are given but no convincing structural correlations

A special study of low-carbon steel as related to automotive sheets was presented by Winlock and Kelley[12] in 1930   This comprehensive but not exhaustive paper indicates the thorough study needed in the successful production of a very common object made of low-carbon steel

Crook and Taylor[13] have studied the hardening and annealing of a 0 20 per cent carbon steel   They find that the martensitization of the pearlitic nodules occurs on quenching from 1350° F , and the uniform absorption of all ferrite at 1550° F   Unfortunately, the 40 very small and indistinct photomicrographs disclose practically nothing at all   They recommend the use of well-deoxidized steel containing over 0 50 per cent manganese as most suitable for "regenerative" material

Crook,[14] alone, writes about the conditions for success in heat-treating low-carbon steels in a paper of recent date   Three excellent photomicrographs illustrate the article   The emphasis is on thorough deoxidization of the steel and the presence of more than 0 50 per cent manganese for "regenerative" heat treatment   One of the prints is of a nonregenerative bessemer steel that has martensitic nodules

The softening temperature of cold-worked low-carbon steel was determined by Publow[15] to be between 1000° and 1100° F   This was in steel for automotive brake drums

Experimental Tests on One Coil of Wire Containing 0 10 Per Cent Carbon

The specific facts and illustrations for the first section of this paper were obtained on cap screws made from a single coil of wire in order to avoid the greater diversity of properties that almost inevitably ensues from using two or more coils   Besides the physical tests on the cold-drawn and annealed wire, and the testing of the 200 cap screws for Fig 1, four distinct series of tests were run

The first series consisted in heating cap screws, in lots of three, to progressively increasing temperatures and quenching in oil or water with hand stirring   The temperatures ranged from 200° to 2000° F. and were obtained in a Hoskins tube furnace of the nichrome resistor

[12] J Winlock and G L Kelley Sheet Steel and Strip Steel for Automobile Bodies *Trans* Amer Soc Steel Treat (1930) **18**, 147

[13] W J Crook and H S Taylor Structure of Heat-treated Low Carbon Steel *Metals & Alloys* (1930) **1**, 539

[14] W J Crook Heat Treatment of Low-carbon Steel *Metal Prog* (1930) **18**, 47

[15] H E Publow Note on the Effect of Various Annealing Temperatures on Cold Worked Low-carbon Steel *Metals & Alloys* (1931) **2**, 18

type   The tube of the furnace was 2½ in inside diameter and 19 in long, giving ample space for a noble metal thermocouple and a long basket of charcoal in the uniformly heated central section of the furnace   Both ends were provided with covers of heavy asbestos board   By using the furnace on end over the quenching tank, it was possible to suspend the cap screws with a looped wire and at the proper time drop the entire string of pieces almost instantly into the coolant   In this series 120 pieces were treated

In the second series of tests the furnace was first brought near some desired temperature and a string of three cap screws was then placed in the furnace for a definite time interval before being dropped into the coolant   The time intervals usually increased from 2 to 10 min in steps of 1 min each and the temperatures of treatment were 1250°, 1300°, 1400° and 1500° F   Altogether, 126 cap screws were treated in this series

A third series of tests consisted in dropping the heated screws in strings of four each from some definite temperature into a large tank of coolant circulated by a centrifugal pump   The pump delivered over 60 gal per minute through a 1-in pipe into a wire basket into which the hot cap screws also dropped from the furnace. Floating cakes of ice held the temperature of the water or 5 per cent caustic solution to near 40° F   In this series 108 cap screws were quenched from temperatures as high as 2300° F

A fourth series of tests was run to study the recrystallization of the cold-upset head of the cap screws   The pieces were held in lots of four for 20 min at temperatures from 995° to 1100° F   and then dropped into water   Only 44 pieces were used in this series

In the four series of tests, over 400 pieces were treated and each cap screw was tested for Brinell hardness on the head and then pulled in the tensile machine   Over 100 pieces were sectioned, smoothed and etched for microscopic inspection. Only the most significant structures were photographed.

None of the tests disclosed such hard and brittle pieces or such soft and brittle pieces as are sometimes encountered in plant practice   Therefore it may be deduced that there are combinations of circumstances that develop extreme properties   It is known that water quenching of low-carbon cap screws after an intended heating to around 1600° F. may give strengths from 50,000 to 120,000 lb. per sq in , yet the series failed to disclose such extremes

Full agreement with Publow was found for the softening temperature of the cold-worked low-carbon steel   Heating to 1000° F   made slight change in the properties, while heating to 1100° F. usually caused much softening and well-developed recrystallization   The sectioned pieces showed many interesting steps in the origin of the new grains and their

absorption of the old deformed stock, until finally they became the typical polygonal grains of fully equiaxed and annealed metal

COMMERCIALLY QUENCHED CAP SCREWS

Manufacturing or commercial demands are such that sometimes a treatment must be given to relieve the brittleness that comes from cold upsetting   One of these treatments is to attempt to heat to around 1600° F , merely bringing the pieces to this heat and dropping them into water. The manufacturer is unwilling to heat higher than necessary because of the heavy scaling, yet desires to anneal and get properties as substantial as possible   He finds that a large percentage of the pieces have passable properties

During the testing of several hundred ⅝-in cap sciews that had been given this treatment, there was opportunity to study the structures as well as the physical properties   Six pieces are selected as covering a rather wide range in both properties and structure and may be presented to complete the outline   Needless to say, the distribution curves of properties were extremely flat and long drawn out, hardly worth reproduction

TABLE 4 —*Properties of Six Cap Screws*

⅝ by 4 in Coarse Threads   Carbon = 0 10 Per Cent

Cap Screw Number	Brinell Hardness	Yield Point, Lb per Sq In	Tensile Strength, Lb per Sq In	Elongation in 2 In (Threaded), Per Cent
1	103	50,050	59,950	18 8
2	131	40,100	63,400	15 6
3	156	62,900	85,700	9 4
4	196	72,800	83,200	3 1
5	174	74,300	89,150	1 6
6	183	74,300	101,550	7 8

The first cap screw listed in Table 4 is very soft, weak, ductile, and is entirely pearlitic. Since it is almost fully annealed it must have been heated close to 1300° F. Higher heat would have left its effect on the pearlite and would have started grain growth. The metal has been relieved of all the effects of cold work and places the specimen at the weakest end of the series   Longitudinal sections at 500 and 3000 dia are given in Figs 11 and 12 and show the typical pearlitic structure

The second cap screw of Table 4 unquestionably reached a higher temperature, for the carbon became dispersed to some extent and on quenching gave rise to the troostitic segregates clearly seen in Figs 13 and 14.   This cap screw is harder, stronger and less ductile than the first one The grain growth was so vigorous as to be determined only on prints of

low magnification; the field of Fig. 13 is wholly within the boundaries of a single ferrite grain.

A condition of less dispersion and greater embrittling effect is found in the third cap screw of the series. The heating started grain growth and
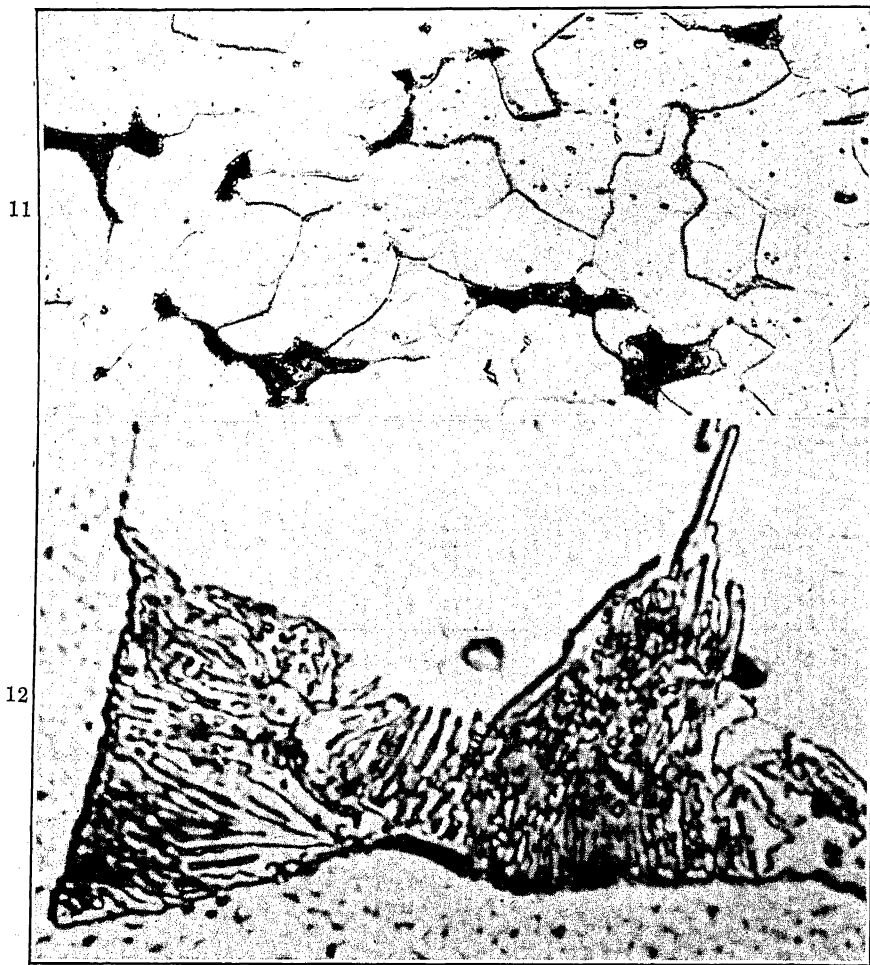
FIG. 11.—LONGITUDINAL SECTION THROUGH CAP SCREW No. 1 OF TABLE 4. × 500. Annealed ferrite and pearlite.

FIG. 12.—PEARLITE MASS IN CAP SCREW No. 1 OF TABLE 4. × 3000. Laminated and granular pearlite in ferrite matrix.

carbon dispersion but the quenching was not sharp enough to hold the nodules to one massive phase, so ferrite and troostite each separated. A structure of this sort obviously is approaching the condition that will manifest properties commonly interpreted as brittle. Although the

FIG. 13.—LONGITUDINAL SECTION THROUGH CAP SCREW No. 2 OF TABLE 4. ✕ 500.
Diffuse rosettes of troostite filaments and ferrite. Entire field is part of one germinated grain of ferrite.

FIG. 14.—ONE OF THE ROSETTES OF FIG. 13. ✕ 3000.
Filaments of troostite in matrix of ferrite. Since nubbly areas do not show discrete particles of cementite they are designated troostite in preference to sorbite or pearlite, both of which should show clearly separated cementite.

FIG. 15.—LONGITUDINAL SECTION THROUGH CAP SCREW No. 3 OF TABLE 4. ✕ 500.
Clusters of troostite filaments in ferrite.

FIG. 16.—ONE OF THE CLUSTERS OF FIG. 15. ✕ 3000.
Although troostite areas appear to have etched in roughened spherulitic outlines, it is questioned whether they are discrete particles of cementite.

piece shows fair elongation in the tensile machine, a shock fracture would doubtless disclose "crystallinity." Figs. 15 and 16 show the structure.

FIG. 17.—LONGITUDINAL SECTION THROUGH CAP SCREW NO. 4 OF TABLE 4. × 500.
Troostitic nodules with ferritic cores in grains of germinated ferrite.
FIG. 18.—ONE OF THE NODULES OF FIG. 17. × 3000.
Ferrite islands and gritty troostite constitute a nodule in matrix of ferrite.

In the fourth cap screw of the series we find greater strength, hardness and resistance to elongation. This is a distinctly brittle bolt. From Figs. 17 and 18 we find that the earlier pearlitic masses have changed to

hard nodules with slight carbon diffusion.   If the white areas inside the
nodule of Fig. 18 are ferrite, as probably they are, the light mottled area

FIG. 19.—LONGITUDINAL SECTION THROUGH CAP SCREW NO. 5 OF TABLE 4.   × 500.
    Troostitic nodules with islands of ferrite in matrix of ferrite.
            FIG. 20.—ONE OF THE NODULES OF FIG. 19.   × 3000.
    Island of ferrite grades insensibly into troostite of increasing carbide localization
(spherulitic but not separated as a distinct phase).

is surely troostite and the darker fringes are sorbite.   The evidence of
grain growth is seen in Fig. 17.

    The fifth cap screw of the series has the lowest ductility of all; it is
softer than the preceding one, which has greater elongation.   From

Figs. 19 and 20 we see the sharply defined nodules and the grain growth. An instructive detail in Fig. 20 is the gradual transition from troostite

FIG. 21.—LONGITUDINAL SECTION THROUGH CAP SCREW No. 6 OF TABLE 4.   × 500.
    Expanded troostitic nodules, usually cored with ferrite or martensite in ferrite matrix.
            FIG. 22.—ONE OF THE MARTENSITIC NODULES OF FIG. 21.   × 3000.
    Island of martensite in low-carbon troostite nodule set in ferrite matrix.

to ferrite along one arm of the enclosed ferritic mass.   If the mottled areas are troostite, there is a gradual transition to the carbonless ferrite of the white headland.

The last cap screw of Table 4 is the strongest of all, it is next to the hardest and has some ductility   The grain growth and carbon dispersion are plain from Fig 21, while Fig 22 gives a picture of a nodule with an unmistakable core of martensite set in a zone of troostite   One is not surprised at the spread and crossed sequence of the physical properties of these cap screws   The resultant properties are dependent on structures of great complexity and individuality   Although the average carbon content was just under 0 10 per cent , it might deviate considerably in local areas or in annular zones   Also, the structures may change greatly from exterior to center, or from side to side of the specimen One is not certain that the properties of the head (hardness) and threaded ends correspond.

The simple cold-headed and untreated cap screw has qualifications not improved upon by a heat treatment producing these diversified structures and properties

Brittleness in Surface-hardened Parts

Low-carbon steel has been used for many years in the manufacture of cyanided or casehardened pins, bolts and set screws   Such pins and bolts often are finished by grinding and provide strong and tough parts that have very hard bearing surfaces   It is generally assumed that such parts shall have tough cores to withstand heavy shocks without fracture.

Much study has been given to the subject of producing the hard exterior and, since it virtually becomes a high-carbon layer, we may pass from that to the matter of insuring a tough core   For one of the most common disappointments is to find that these surface-hardened parts break with a short and brittle fracture

The subject promptly ramifies into widely separated topics like the methods of testing, the details of manufacture, compositions, wire-drawing details, rolling-mill procedure and even the making of steel and the treatment of ingots   But since the structures and properties already presented appear to possess a degree of finality, this very large subject may be approached from this particular point of view

One preliminary statement should be made regarding the difference between casehardening low-carbon steel and iron   Wrought iron was used for this purpose long before low-carbon steel was invented and wrought iron has always made a very soft and tough core   When a piece of casehardened wrought iron is struck a sharp and heavy blow, the case may crack in many places but the core holds tenaciously and bends but does not part   Quenchings make comparatively little difference in the plasticity of wrought iron   But if steel is substituted for the iron an entirely different material is being used   Low-carbon steel may replace iron for many purposes but its carbon content gives it new prop-

erties when quenched   We know of no way to give wrought iron the
brittleness easily imparted to a 0 10 per cent carbon steel

It is generally known that a cyanided or casehardened part may be
either tough or brittle   The factors that determine the sort of fracture
that results on testing are chiefly the following (1) hardness of core, (2)
brittle component in core, (3) temperature of testing, (4) suddenness of
blow, (5) thickness of case, (6) hardness of case

It will probably be granted that the harder the core, the greater the
tendency toward brittleness, yet this is only a general conclusion.
A cyanided bolt with core hardness of Brinell 143 broke with a brittle
crystalline fracture, while a heavily cased wrought iron bent 90°, although
its core hardness was Brinell 156   Some casehardened steel was found
tough at Brinell 179 and other pieces were brittle at Brinell 163, but in
general the tendency is for brittleness to accompany hardness and
toughness to increase with softness   A wire with Brinell 126 made very
tough bolts with core hardness of only Brinell 121, and another wire that
was Brinell 163 made brittle casehardened bolts that had core hardness
of Brinell 187

A brittle component in the core may be expected to make a part
brittle to a shock test   Either hard nodules from transformed pearlite
or spots of low-carbon martensite will provide the means for a crack to
propagate   If the carbon is high enough to form martensite on quench-
ing, or if the quenching is from the temperature of nodule formation with
concentrations of carbide already present, brittleness may be expected
The general remedy for brittleness in cyanided parts of small section
is merely to reheat in the bath and quench from a higher temperature
This simply gives more carbide dispersion and avoids the embrit-
tling concentrations

The temperature of testing is very important   Even very tough parts
are brittle if the temperature is lowered enough, and conversely, short
and brittle fractures may become tough if a piece is first made warm, or
hot, as held in the hand   This is widely known for steel in general and
applies equally well to surface-hardened parts

The rate of the application of pressure may easily be the sole deter-
mining factor as to whether a part is brittle or not   This is fairly well
known in the general mechanics of the metals but becomes a critical
factor in testing surface-hardened parts   A common method is to
support the ends of pins and bear down on the middle with a screw press
Tough cores are supposed to hold the bent part even after the cracks
start in several places   If a core is very brittle the part snaps across
with slight permanent deformation, that is, the piece appears straight
when the fractured ends are again matched   In the sledge test one end
of a bolt is held rigidly and the other struck a smart blow with a
sledge hammer   This is an exacting test

Although the apparent brittleness of a core increases with the thickness of the case, it does not follow that thin cases insure toughness. Steel can be brittle even if it is not surface-hardened and originally very tough steel may be made very brittle after receiving only a few thousandths of an inch of hard case

Naturally, the harder the case the greater the apparent brittleness of a core due to strain concentration at one crack in the case   Even impossibly brittle cores will appear tougher if the case is softened so that the strain is dissipated over an increased area

All of these factors together have little meaning if a core is soft and plastic or relatively hard and full of some stiffening component   In either instance, the condition is far from some indistinct border line   At many intermediate stages the manipulation of a factor will determine the result

All of the experiments recorded in the first part of the paper offer direct evidence that a soft core is insured by low carbon in the steel   If the carbon is on the low side of the range, a reheat and quench from even the nodularizing temperature might make a passable core, other factors being favorable, but with the carbon as high as 0 09 or 0 10 per cent or higher, there enters the danger of lack of toughness   And with the carbon as high as 0 16 per cent or higher there is the probability of brittleness from a high-temperature water quench as well as from a lower reheat temperature   Expressed in degrees, the parts very low in carbon might be quenched from the box at 1750° F with toughness   When reheated to 1440° F and quenched they should again be tough, but if the carbon is as high as 0 10 per cent there should certainly be toughness at the 1750° F quench and lack of it at the 1440° F quench   Reheating to this extent has allowed much segregation of the previously dispersed carbide

Metallurgists generally have held that reheating to 1425° F , at least, is necessary to produce the required casehardness, but at this temperature the coalescence of both carbide and ferrite is rapid, the dispersed troostite condition is rapidly changing to the nodular.   Preliminary experiments indicate that it is not necessary to reheat to this temperature but that 1380° F is adequate for casehardness   If hardness can be obtained at 1330° F , the cores should be still tougher, for the lower the temperature, the less segregation there is of the dispersed carbide   This is simply the matter of reheating to above the lower critical instead of to above the upper critical temperature of the hypereutectoid case

If other factors in the technique of making steel can insure tough cores, they have not made themselves generally known.   It has been suspected that some component or peculiar structure might induce
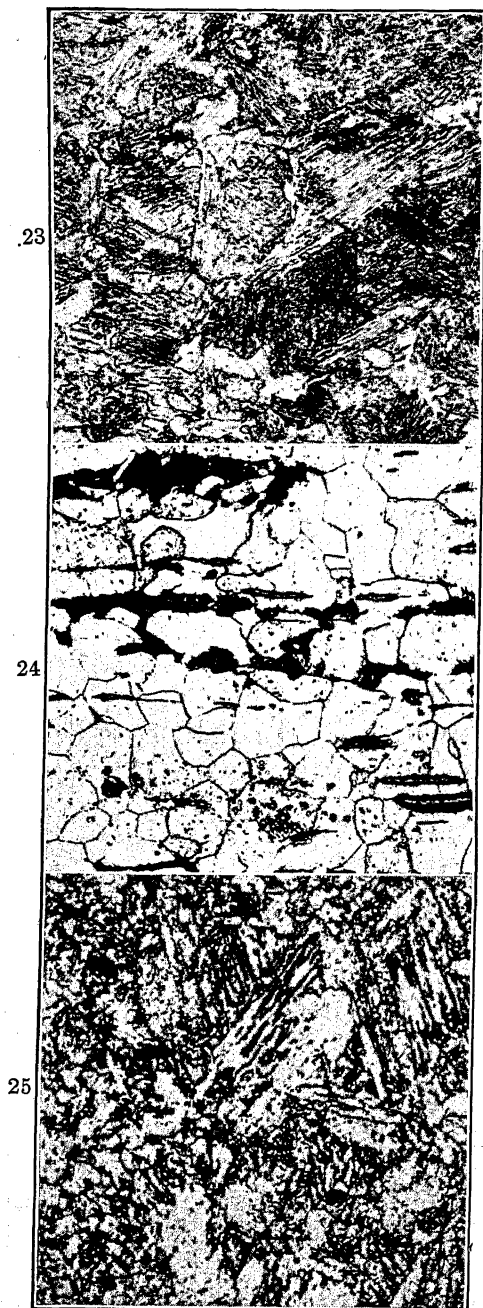
FIGS. 23–25.—CAPTIONS ON OPPOSITE PAGE.

a harder ferrite grain, one more easily ruptured during shock. Microscopic search has not revealed any evidence of this possibility.

An interesting but unsatisfying experiment is to produce entirely different fractures only an inch or so apart on the same piece of steel, by manipulation of one of the determinants of the fracture. One end can be made bright, coarse grained and crystalline; the other end can be made dull, rough and irregular.

A matter of considerable significance is that bessemer screw stock, notably S.A.E. "1112," is not particularly susceptible to brittleness. Either as first quenched from the box or after a 1440° F. reheat it usually gives a rough and tearing fracture. The ends are commonly dull and jagged, with splits and a fibrous texture. This is the material that Crook regards as being "unregenerative," or having its carbide undiffusible.

The author has been unable to find that the carbide in screw stock does not diffuse. A piece of 1¾-in. hexagonal "1112" that was Brinell 179 as received was quenched from 1650° F. in cold 5 per cent. caustic. The outside of the piece was Brinell 302 and the center 196. The structure of the interior is seen in Fig. 23. That there has been extensive "regeneration" carbide diffu-

sion requires merely comparing with the original structure (Fig 24), where the ferrite and pearlite are sharply defined

A transverse section through the core of a tough screw stock bolt is given in Fig 25 Although it shows a rather coarse texture, and in other fields some spots of original ferrite, the structure closely resembles that which has been called the "dispersed troostite" condition Screw stock acts more sluggishly than basic open-hearth steel in reaching equilibrium conditions It is foul with sulfides, slag and oxides, microscopic patches of the original ferrite are commonly found after the usual treatments Apparently its very defects give it the much desired toughness after casehardening It stands between the impossible genuine wrought iron and the over-quickly responding basic low-carbon steel

SUMMARY

If we have in mind a 0 10 per cent carbon steel and consult the usual iron-carbon diagram, as the most recent one by Harrington and Wood,[16] we see that on cooling from above the upper critical range ferrite begins to separate at about 1635° F On further cooling ferrite separates rapidly, so that at 1270° F the carbon has concentrated to eutectoid proportions and is ready to separate into the aggregate of cementite and ferrite known as pearlite At this final concentration the matrix for pearlite composes some 12 per cent of the total mass At the intermediate temperature of 1440° F the separated ferrite has amounted to only some 30 per cent and the carbide-bearing matrix is about 70 per cent of the mass The essential part of this paper deals with the variety of the structures that may be obtained on quenching from above and within this critical range

Roy H Smith appears to have been the first to obtain sensibly entirely martensitic structures by a forced quench from above the critical range, but he did not follow up the investigation to account for the brittleness of the steel as quenched from within the critical range This has now been done, so that numerous prints show the dispersions, spangles, rosettes, cored nodules and hard aggregates that are obtainable.

[16] R H Harrington and W P Wood Critical Ranges in Pure Iron-Carbon Alloys *Trans* Amer Soc Steel Treat (1930) **18**, 632

FIG 23 —LONGITUDINAL SECTION THROUGH 1¾-IN HEXAGONAL SCREW STOCK QUENCHED FROM 1650° F INTO 5 PER CENT CAUSTIC × 200
Brinell hardness, 196 Higher magnification would be required to designate exact structure between white ferrite spots Carbide diffusion has been extensive
FIG 24 —LONGITUDINAL SECTION THROUGH ORIGINAL BAR OF SCREW STOCK × 200
Ferrite and pearlite sharply defined Sulfides, slag and oxide inclusions are prominent
FIG 25 —TRANSVERSE SECTION THROUGH TOUGH CASEHARDENED BESSEMERS CREW STOCK × 250
There has been extensive carbon dispersion and final structure is of dispersed troostite type

There is a wide temperature interval from near the upper critical it may extend from 1600° F to above 2000° F , where a water or oil quench produces a rather uniform mixture of ferrite and carbon-rich concentrate, which tentatively has been called dispersed troostite   This mixture has greater strength than the cold-worked metal that results when cap screws are made from cold-drawn wire, but its yield point is lower   A cold-formed cap screw is thus difficult to improve upon by heat treatments, for either brittle structures or structures having lower yield points are encountered

This dispersed troostite structure is also the one produced when low-carbon steel is casehardened and quenched from the box   Its high ductility makes it naturally suitable for producing tough cores

On the other hand, reheating either a quenched or annealed casehardened piece to 1440° F and expecting a tough core is not in line with equilibrium conditions and runs contrary to a great deal of plant experience   In pieces of small section, one might expect some sort of hard nodule or spiked rosette that would make the piece brittle, especially by the more exacting tests   The reasons for proposing a reheating temperature some hundred degrees lower have been given   The problem is to get a hard case before carbon segregation causes brittleness

The finding of tough cores after grinding off the cases from brittle pieces is attributed to uncritical testing   An extensive lack of detailed information about the microscopic structures appears to be the basis on which so many authorities recommend the usual double heat treatments The higher magnifications quickly disprove the statements that the structure after a high-temperature quench resembles the original pearlitic steel, or that quenching from 1430° F causes no appreciable change after a quench from 1625° F

Basic steel containing 0 10 per cent carbon may be expected to caseharden and have a tough fracture on quenching from the box, its structure will be similar to that seen in Fig 26   On reheating and quenching from 1440° F the fracture is rather brittle and the structure distinctly nodular, as in Fig. 27   The original wire, in which the fracture made by a hammer blow at a notched end is very finely crystalline, is easily made coarsely crystalline and highly brittle by heating to 1625° F , cooling to 1325° F and sharply quenching in water   Such treatment gives the structure seen in Fig 28   The original ferrite grains have germinated, the carbide segregated during the slow cooling and the quenching of the carbon-rich nodules left them cored with martensite   Reheating to 1000° F. or over will allow the separation of ferrite and its start at coalescence as seen in Fig 29   More thorough annealing is prone to allow the coalescence of massive cementite, which with pearlite is commonly found in these steels after quenching and annealing

FIG. 26.—CORE OF CASEHARDENED 0.10 PER CENT. CARBON STEEL AS QUENCHED FROM BOX. ✕ 1000.

This structure is tentatively called dispersed troostite. It has a tough fracture.

FIG. 27.—SAME AS FIG. 26 AFTER REHEATING AND QUENCHING FROM 1440° F. ✕ 1000.

It has become nodular and gives a brittle fracture.

FIG. 28.—SECTION THROUGH BRITTLE AND HIGHLY "CRYSTALLINE" WIRE. ✕ 1000.

This piece was heated to 1625° F., cooled to 1325° F. 20 min., then quenched. Martensitic nodules have formed abundantly, especially at borders of germinated grains.

FIG. 29.—FERRITE FORMING AND COALESCING THROUGHOUT SPOT THAT WAS PREVIOUSLY A HARD NODULE. ✕ 1000.

Piece with structure of Fig. 28 was merely brought up to temperature of 1250° F.

Thus, as far as the present studies warrant conclusions, a cold-formed cap screw has the best combination of properties and a single quenched casehardened part will have the toughest core. But the subject is a very large one and warrants a great deal more detailed study. Present statements but suggest further inquiries.

FIG. 30.—MARTENSITE, PEARLITE AND "BETWEEN STRUCTURES" IN 0.10 PER CENT. CARBON STEEL AFTER QUENCHING AT 1310° F.   × 2000.

As regards the dispersion and segregation of the carbon, are there factors besides temperature that influence this action? What is behind Crook's statement that thorough deoxidization and high manganese is essential to dispersion? Many millions of tough casehardened screw stock parts are in use today. This fact and the experiments recorded here appear in direct conflict with his conclusions.

And as regards the low-temperature quench of parts previously given a dispersion quench, is it commercially practicable to harden the case and make the core tough in the same part? The reheat to 1440° F.

has much against its feasibility, with no authorities holding for one hundred degrees lower in temperature   Are we mistaken in the structures and properties, or cannot furnaces be operated within the close limits required of the lower range?

And what are the intimate facts about tough cores in steel containing 0 20 per cent carbon? Will not a high-temperature water quench give much martensite, and if an oil quench is used will not a reheat to 1440° F surely give brittleness?   Can a 1340° reheat be used with this steel?

And, after all, is it essential for hardness or wearing quality to have a refined case?

The designations of troostite and sorbite for the dispersions and nodules will surely arouse conflicting emotions   In fact, Lucas[17] has just stated that troostite is very fine pearlite   At present the author holds to the designations given because the separation into discrete particles of cementite and ferrite does not appear to him to be a completed fact   It is rather a matrix, separated from the ferrite, already spherulitic with nuclei rich in carbide, but not yet two distinct phases of carbide and ferrite   Unquestionably the troostite often shows concretions or carbide-rich nubbles, and the sorbite even more so   The darker and more pebbly areas in Figs 14, 16, 18, 20 and 22 are far less sharply cut into distinct components than the pearlites of Figs 3, 4, 6 and 12

A further reason for holding this phase as something else than normal pearlite is that it is a product of high-temperature quenching   It disagrees with our conceptions of pearlite separating on slowly cooling through 1325° F , or lower, to call this quenched segregate by the same name

Fig 30 presents a curious condition, where one extreme of a pearlitic mass was transformed to massive martensite by quenching from just above 1300° F   At the top of the figure is a triangular mass of martensite, heavily in relief, at the lower extremity is unaltered pearlite   In the narrower connecting zone in the middle is a region of "between structure," neither martensite nor pearlite   And all of these pictures are but samples of the structures in the heat-treated low-carbon steels

DISCUSSION

(Edgar C Bain presiding)

G B WATERHOUSE, Cambridge, Mass —There is merely one question I want to ask   That is, whether the rather unorthodox methods of preparation of samples that Mr Pulsifer presented in his book some years ago were used in preparing these photomicrographs shown today, and if he will take a few minutes to tell us how he prepared these specimens that we have seen at 1000, 2000 and 3000 diameters

[17] F F Lucas On the Art of Metallography   See page 44

H B Pulsifer —The specimens were prepared by my usual Bolshevistic method of very quick surfacing and then ordinary etching in picric acid solution The slides that were shown were never really polished, but smoothed down on several grades of paper, French emery paper, after filing, rubbed on a little carborundum paste on a hand board for a few seconds, then slightly etched in the picric acid solution That gives a tooth for the finer smoothing on tripoli paste, which smooths the material quickly, since it is somewhat etched and has a certain roughness

Ordinary steel and iron is not easily attacked by the ordinary tripoli, because it is a little too hard, but if it is etched, it smooths off quickly After that has been done once or twice, the material can be given a final etch

It is a very quick operation One of the men in the plant brought a specimen into the laboratory the other day He did not think I could tell him soon enough for practical use how much carbon there was I cut out a piece and had it under the microscope to show him the carbon in about three minutes It was a pretty good surface, a very clear structure

N A Ziegler, East Pittsburgh, Pa —I congratulate Mr Pulsifer on his splendid photomicrographs I would like to ask how he can avoid pitting in polishing partly etched samples Usually when I attempt to do that and then look at the sample through a microscope it looks like a bad case of smallpox to me

H B Pulsifer —I think Mr Ziegler had better explain how he gets the pits

Yap, Chu-Phay —There is one point in the paper that I would like to comment on, because about five years ago I did some work in low-carbon steels This is the experience I had If you anneal slowly you will find that most of the cementite will be along the grain boundaries, so structurally one will be a higher carbon steel than the other When you quench, this will be preserved as martensite, and so the intercrystalline boundary will be quite brittle That is probably one reason why it gives a brittle structure I wonder if Mr Pulsifer would care to comment on that

H B Pulsifer —I think any one who has worked with these low-carbon materials, and the results of quenching, will agree with me that the migration of the carbon is excessively rapid, and the result depends on times that should be measured in the hundredth, or so, of a second The structures are often extremely different from causes which might easily be overlooked, especially as to the rate of cooling

What you are going to get and how the carbon is going to be distributed is like looking at a picture book The variety of structures is very great—all kinds of interlacing ferrite grains and martensitic spots in peculiar groupings

There is a paper to be given by Mr Bates[18] this afternoon showing some nodules I do not think he mentions the subject of these nodules, but he has some of my typical structures in his paper, and some of the typical interlacing ferrite fingers

There is one interesting thing about this which is exactly in line with what Mr Yap mentions That is that on the annealing of one of these nodules the ferrite coalesces into a massive groundmass, and the cementite comes out in little globules all through it That is a characteristic structure, which is illustrated in the paper, I think, but not shown on the screen Where there was a nodule we get a new area of ferrite with little cementite particles all through it

If a little more time is given for the annealing and the coalescence it is easy to get massive cementite and massive ferrite

In closing the discussion, which has taken an unexpected turn toward the surfacing of specimens and delineation of structure, may I say that better and better results

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[18] A A Bates. Aging in Low-carbon Steels Amer Soc for Steel Treat 1931

are continually being obtained without resorting to an elaborate polishing of the specimens

The most recent accomplishment is in learning how to etch so as to obtain sharp boundaries about ferrite grains without overetching pearlite   This is virtually the etching of grain boundaries in massive pearlite, which has not always been easy to do   Unfortunately, this seems to require a rather long etching time and so does not add anything to the speed of preparation, but the results are interesting.

Bright Annealing of Steels in Hydrogen

By Floyd C Kelley,* Schenectady, N Y

There is an ever-increasing demand for furnaces with controlled atmosphere, due to the large quantities of steel being used in the automotive industry, such as the high-chromium stainless irons, the 18 Cr, 8 Ni stainless iron and low-carbon steel sheets

The difficulties involved in the annealing of such materials, if they are to be kept absolutely free from oxidation, are many   It is possible to bright-anneal these steels in small laboratory hydrogen furnaces, using specially purified hydrogen and taking some additional precautions

In the first place, the insulation, usually of alumina or magnesia, holds small amounts of water vapor, which it is almost impossible to remove completely   Secondly, there is always condensation of water vapor in the cooling chambers of such furnaces, and with the continuous circulation of the hydrogen gas in the furnace, the water vapor is carried from the cooling chamber back into the heating chamber   This water vapor oxidizes the charge.   Lastly, the supply of moisture is made sure by the diffusion of small amounts of air from the atmosphere into the furnace against the pressure of the hydrogen.   The oxygen combines with the hydrogen and forms more water   Under such conditions there is little gained by using specially purified gas, because it becomes contaminated after reaching the furnace

Low-carbon Steel

If a sheet of low-carbon steel is annealed in such a furnace at 750° C and allowed to cool with the furnace, an adequate flow of purified hydrogen being maintained all of the time, the steel will come out with a very thin coating of blue oxide   If a similar sheet is annealed at the same temperature and quickly pushed into the cooling chamber, it will come out nearly bright, or perhaps with only the edges slightly discolored   It is difficult to get a piece of steel through a furnace of this type with an absolutely bright surface   This is due to the fact that there are always traces of oxygen or water vapor in the furnace   When the steel is allowed to cool with the furnace, it reaches a critical temperature where the affinity of iron for oxygen is greater than that of hydrogen for oxygen, and the steel comes out discolored.   If the steel is pushed from the hot zone

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into the cooling chamber, it passes through the critical temperature range so rapidly that it does not have time to pick up much oxygen to discolor it, except at the edges where it is in contact with traces of moisture condensed on the wall of the cooling chamber.

STAINLESS IRON

Commercial hot-rolled stainless iron has a brown surface Similar iron annealed in the laboratory furnace and either allowed to cool with the furnace or pushed into the cooling chamber comes out a dark green color   In other words, where there is ample oxygen the iron oxide gives the predominating color, but where the supply of oxygen is limited, as in the hydrogen atmosphere, the chromium, being more active toward oxygen than either hydrogen or iron at the annealing temperature, takes all of the oxygen and gives the iron the predominating green of chromic oxide   This is true whether the steel is slowly cooled or pushed quickly into the cooling chamber   In fact, the chromium oxidizes at a temperature at which iron oxide could not exist, and forms a protective oxidized layer of chromic oxide over the iron just underneath   It is possible to reduce the dark brown oxide on a hot-rolled stainless iron sheet in the laboratory furnace without any special precautions   The surface seems to be composed mainly of iron oxide due to some selective oxidation

METHODS OF PROTECTION AGAINST OXIDATION

It is possible to anneal low-carbon steels in a hydrogen furnace of the laboratory type and have them come out absolutely clean and bright, by wrapping the material in thin sheet-iron ribbon, being careful to allow each turn to overlap well the one next to it   It may also be enclosed by a seamless steel tube closed at both ends by a piece of thin sheet iron made tight by wiring it fast   Steel annealed in this manner may be cooled with the furnace without oxidation, because the iron tube or sheet with which it comes into contact takes all of the oxygen from the hydrogen before it enters the enclosure on cooling down

The stainless iron acts in quite a different manner, because, as shown above, it is capable of holding the oxygen at the annealing temperature where iron would be reduced. A few illustrations will make this clear.

When wrapped in iron ribbon or put into the seamless steel tube, the material comes out with a thin coating of chromic oxide. If the first tube is placed inside a second tube closed in a similar manner, the sheets still come out green   This point illustrates the extreme activity of the chromium in the iron and shows that oxygen or water vapor diffuses inside the closed iron tubes

After obtaining this information, the next step was to enclose bright sheets of chromium iron in a tube and pack it in a second tube, using a mixture of 50 per cent of powdered chromium and 50 per cent of powdered alumina   The details are shown in Fig 1   The ends of the second tube were closed as before, and the whole charge was annealed at 1100° C These sheets came out perfectly bright and clean, with a silvery luster

Since two powdered materials had been used simultaneously in this experiment it was necessary to eliminate one of them to be sure that our data were complete   A second lot of sheets was fired in the same way but alumina alone was used for the packing material   The sheets came out green

This experiment proved conclusively that the powdered chromium was taking care of all oxygen and moisture which might otherwise have diffused into the chamber enclosing the metal sheets   By analogy it was assumed that other metal powders capable of retaining oxygen in a

2-Furnace Box	6 - Wire
3-Steel Tube	7-Steel Tube
4-Stainless Steel Samples	8-Alumina and Chromium Powders
5- Steel Cap	9-Steel Cap
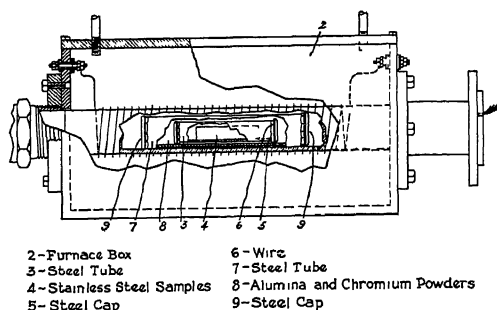
FIG 1 —SHEETS OF STEEL PACKED FOR ANNEALING

hydrogen atmosphere at high temperatures might be used instead of chromium, so the following were tried with equal success   Alumina plus 10 per cent of aluminum, alumina plus 10 per cent of manganese, alumina plus 10 per cent of silicon, alumina plus 15 per cent of ferrosilicon, alumina plus 15 per cent of ferrovanadium, and so on

The next experiment was made to determine the activity of the hydrogen that finally reached the inside of the innermost tube   Strips of the oxidized 18 per cent chromium iron and of 18 per cent chromium, 8 per cent nickel iron were placed inside a closed tube as before and then packed in a second tube surrounded by alumina plus chromium   They were fired at 1200° C for 1 hr and then pushed into the cooling chamber These sheets came out perfectly clean and bright, but had a matte finish   The dark green oxide had disappeared   This happened in a chamber where there could have been very little circulation except by diffusion and showed that the chromic oxide had been reduced by the hydrogen.

Continuous Annealing of Metal Strips

Much of the demand for these materials is in strip form for which continuous annealing operation is desirable   The next procedure was to apply the knowledge already gained to a continuous annealing operation

Split graphite stoppers with a slot milled in one-half of each stopper, just large enough to allow the ribbon to slip through easily, were provided for the heating and cooling ends of the 5-in hydrogen tube furnace used

Then a seamless steel tube was cut long enough to extend from the graphite stopper at the end next to the cooling chamber, just into the hot zone of the furnace chamber itself   At one end was welded a slotted steel disk about ⅛ in thick.   The slot had a clearance of about 0 010 in , to allow the ribbon to pass through easily   A flange was welded to the other end and a similar slotted steel disk provided with holes so that it could be made fast to the flange by screws   A suitable gasket was used

1-Furnace Box	6- Water Jacket	12-Graphite Stopper	17- Steel Ribbon
2-Heating Chamber	8- Water Outlet	13-Slotted Disk	18⎫ Gears
3-Cooling Chamber	9- Hydrogen Inlet	14-Graphite Stopper	19⎭
4-Alundum Tube	10- Slotted Graphite Stopper	15- Slot	20-Motor
5-Winding Molybdenum	11- Steel Tube	16- Spacer	21- Gear
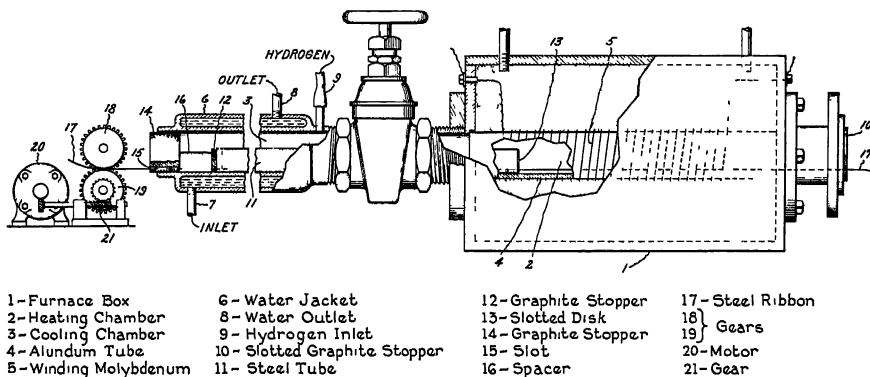
FIG 2 —APPARATUS FOR CONTINUOUS ANNEALING OF METAL STRIPS

to make the joint between the flange and the disk   This construction allowed the ribbon to be pushed through the slot in the closed end at the front and out through the open tube at the back   Then the ribbon could be pushed through the slotted disk at the back end and the disk and gasket made tight by the screws   The tube and ribbon were then pushed into place in the furnace   The tube was supported by metal supports to bring all of the slots in alignment   The split graphite stoppers provided with the slots were inserted over the ribbon at either end of the furnace and the furnace was brought to the annealing temperature.

The ribbon to be annealed was put on a reel at the front of the furnace and was drawn through the furnace by a pair of rubber-covered rolls operated by a small motor through suitable reduction gears.   The set-up is shown in Fig 2

The hydrogen used in these experiments was supplied to the furnace alone, and was purified by passing through a sulfuric acid bubble bottle

over copper gauze heated to 600° C , through another bubble bottle at the exit end of the copper purifying furnace, then through towers filled with small pieces of metallic sodium and finally over phosphorous pentoxide

The low-carbon steel ribbon was pulled through by hand in a preliminary experiment, to determine just how long it had to stay in the 20-in hot zone of the furnace to secure the proper anneal   It was pulled a distance of 8 in and then allowed to remain stationary for a period of 10 min   This was repeated every 10 min   The ribbon was discolored over a narrow zone every 8 in   Measurement showed that this discoloration occurred just inside the closed iron tube at the hot end   When it was pulled at the rate of 1 in per minute, the discoloration disappeared and the strip came out bright   The discoloration was due to diffusion of the impure hydrogen of the furnace through the clearance space around the ribbon, and occurred at the point on the ribbon where it reached the critical temperature for oxidation   Increasing the rate at which it was drawn through the tube did not leave any portion of it near the slot, where diffusion took place, long enough for the ribbon to become noticeably oxidized   The dead atmosphere of the closed tube did not allow much circulation or diffusion and the ribbon came out bright It was finally found that if the ribbon was drawn through the furnace heated to 750° C at a rate of 1 ft per minute with the rolls, it was soft and perfectly bright   Its hardness in the cold-rolled state was 105 Rockwell B, extended scale, and after anneal it was about 55 Rockwell B

In order to check the previous data, an experiment was tried using stainless iron, but this came out green in color, as was expected   It had already been found that if the steel was once heated in the open furnace to the point of oxidation it could not be reduced by any ordinary means

Continuous Annealing of Stainless Iron

The next experiment was modified to meet the condition previously found necessary   The set-up is shown in Fig 3 where two furnaces are used   The upper furnace contains a seamless steel tube filled with alumina plus 25 per cent of powdered 50 per cent ferrosilicon   The hydrogen inlet end is in the cooling chamber of the furnace, it is provided with a rubber stopper through which extends a $\frac{3}{8}$-in copper tube, which extends out through a similar stopper in the end of the cooling chamber A $\frac{1}{4}$-in pipe is welded to the exit end and extends out of the front end of the furnace

The lower furnace is provided with a seamless steel tube which extends from the projection on the front to within about 4 in of the stopper at the back   There is a spacer between the end of the tube and the slotted graphite stopper in the back end of the furnace   This is used to avoid the necessity of having the slots in perfect alignment   The tube is provided with slots at either end, as described in the previous

experiment   About 12 in from the front end at the top of the tube, a small ¼-in seamless steel tube is welded to provide an inlet for hydrogen This tube extends out through a hole in the slotted graphite stopper in the front end of the furnace and is joined by a union to the ¼-in pipe extending out of the upper furnace   The ribbon is threaded through the tube as described in the previous experiment   Purified hydrogen is passed through the tube, which is filled with powdered alumina plus ferrosilicon heated to 900° C in the first furnace   Then it passes into the annealing tube in the second furnace, which is heated to 1100° C   The

1-Furnace Box
3-Heating Chamber
4-Cooling Chamber
5-Entrance Chamber
6-Rubber Stopper
7-Graphite Stopper
8-Steel Tube

10-Alumina and Ferrosilicon
11-Pipe
12-Rubber Stopper
13-Steel Tube
14-Steel Tubing
15-Slotted Steel Disk
17-Hydrogen Inlet

17A-Spacer
18-Steel Ribbon
19⎫
20⎬Gears
21⎭
22-Motor
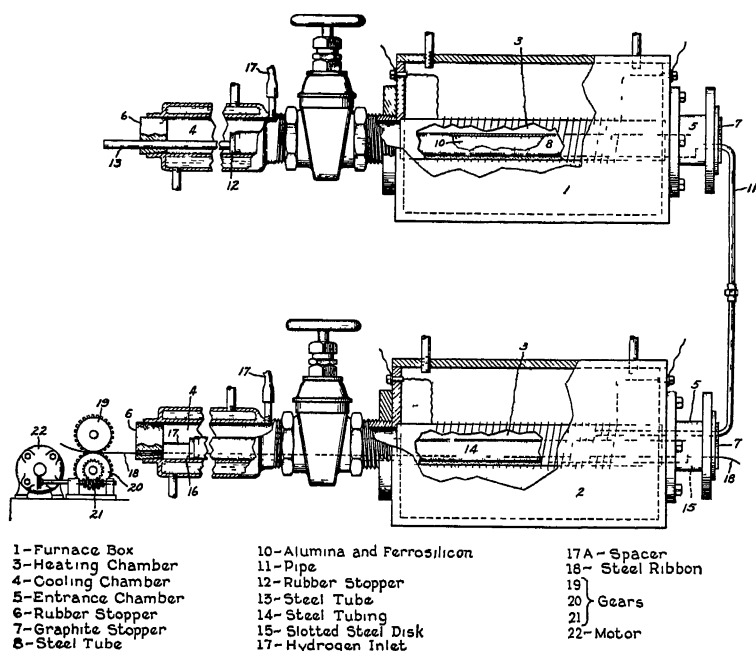
FIG 3 —APPARATUS FOR CONTINUOUS ANNEALING OF STAINLESS IRON

rate of flow of the hydrogen is 2 5 to 5 liters per hour   Both tubes are enclosed by the hydrogen atmospheres of their respective furnaces

The stainless iron ribbon enters the furnace through the graphite stopper and then goes through the slot in the cold end of the annealing tube before it becomes heated   The ribbon is drawn through this tube at a rate of 2 ft per minute, as in the previous experiment, but emerges at the cooling chamber end with a perfectly bright, silvery luster   Its Rockwell B hardness drops from 110, on the extended scale, in the cold-rolled condition to 71 Rockwell B after annealing.   Its color is lighter and its appearance brighter when compared with the cold-rolled material This is probably due to grain growth during annealing, resulting in a change of the character of the reflected light

Under the above conditions, the last traces of oxygen and water vapor are entirely removed while the hydrogen is passing through the tube of heated ferrosilicon powder   The hydrogen enters the annealing chamber of the second tube free from oxygen or moisture   There is just enough pressure of hydrogen in the annealing chamber to limit diffusion of the furnace atmosphere through the clearance space around the ribbon at the ends of the tube   If small amounts should get in, the oxygen would be cleaned up by the walls of the iron tube at the point where the critical temperature for the oxidation of iron exists   It is probable also that very small amounts could give a transparent film of oxide on the surface of the sheet, which could not be detected

CONCLUSION

The fundamental principles outlined, and described for the laboratory type of furnace, would apply equally well to furnaces of a larger type The construction of larger equipments, of course, presents unusual problems due to the necessary high temperature used in the annealing of stainless iron   The maintenance of a pure atmosphere is of utmost importance, and it has been shown on a small scale that such an accomplishment is possible

DISCUSSION

(R F Harrington presiding)

G B WATERHOUSE, Cambridge, Mass —I should like to ask about the electrolene

F C KELLEY —We have not tried electrolene under the conditions used in bright annealing stainless iron, but I think from the results already obtained that probably it would result in oxidation of the material   I ought not to make this statement at this time because I have not tried the experiments, and I am not sure, but if these preliminary experiments mean anything I certainly would not expect to be able to bright anneal the stainless iron in electrolene without the removal of CO_2 and traces of water, but cold-rolled iron can be bright annealed because the equilibrium conditions are such that it is possible to heat it to 900° C , or 750° C , and bring it out absolutely clean if it is cooled quickly enough or if it is cooled in an iron tube such as was shown in Fig 2, where the atmosphere in the closed tube has been cleaned up by the walls of the tube itself

Electrolene is a gas produced by cracking up city gas, that is, the city gas is put through a furnace heated to about 1000° and steam-blown into the city gas at this temperature, which causes a breakdown   The final product is about 75 per cent hydrogen, as I remember it, with about 19 per cent CO, and small amounts of CO_2, nitrogen and methane

G D BOYD, Wallingford, Conn —The paper presented by Mr Kelley has brought out many interesting points regarding the annealing of chromium-bearing steels in controlled-atmosphere furnaces   The facts described in his paper have been substantiated by the Wallingford Steel Co , which has had in operation for the past six months a large furnace designed for the annealing of chromium steels in commercial quantities

Our furnace is designed for use with controlled atmosphere, such as hydrogen, carbon monoxide and nitrogen, and to anneal strips as wide as 13 in. continuously. In spite of all the precautions that we may take to dry and purify our gases, we are not able to produce a strip of chromium-bearing steel that is entirely free of oxide. When annealing the 18 chrome, 8 nickel steel in a pure hydrogen atmosphere, we produce a light green oxide on the surface of the strip, which is readily removed by pickling, with a negligible loss in weight. When annealing the 16 to 18 chrome steel, the oxide is more of a bluish tinge. We have also discovered that the character of the oxides formed is changed only a very little by the use of a gas composed of about 30 per cent CO and 70 per cent N, which we manufacture in a producer with coke as a fuel.

Since we are able to treat ordinary cold-rolled steel in this furnace and get it absolutely bright, and also nickel silver, pure nickel, some grades of brass and phosphor bronze, it is clearly demonstrated, as Mr. Kelley reports, that the chromium steels are extremely susceptible to attack by even the slightest amounts of oxygen and moisture at elevated temperatures. We have been operating our furnace a little more than six months on a production basis, and are glad that these experiments are being carried on and hope that some more important factors will be discovered.

A. B. KINZEL, Long Island City, N. Y.—Mr. Kelley has given a solution to a problem that has a great deal of practical interest, and it seems that the method should be satisfactory on a commercial scale for continuous annealing. However, the problem becomes more difficult when pack annealing is considered, and there are still some phases that will have to be worked out in that connection.

I should also like to comment on the annealing of plain carbon steels. Such steels, as well as nonferrous materials, may be annealed satisfactorily in the usual commercial cylinder nitrogen with a comparatively simple purification train. Commercial applications have shown that bright annealing can be successfully carried out with this gas. It has the unique advantage of completely eliminating the problem of decarburization, which is so bothersome in the case of the higher carbon steels.

F. C. KELLEY.—Mr. Boyd has brought out one point of striking difference between the 18 chrome, 8 nickel steel and the straight 16 to 18 chrome steel, and that is the difference in the color of their oxidized surfaces, after annealing in his commercial type of furnace. This difference in color of oxidized sheets is due, I believe, to selective oxidation at different temperatures, as stated before, but conditions vary with the different furnace designs and one would have to make a close study of the conditions to determine just what occurs in the particular case referred to. The samples that I have with me are absolutely bright and clean; and that is exactly what is desired. The steel has nearly a mirrorlike surface and very little work has to be done in polishing to secure the desired finish. The bright-annealed strip is desired without traces of oxidation present on the surface.

Development of Continuous Gas Carburizing

By R. J. Cowan,* Toledo, Ohio

In the art of cementation a controversy has been going on for years as to whether solid or gaseous carbon is the active agent in carburizing steel More recently opinion has crystallized into a compromise to the effect that carburizing is a gaseous cementation of steel in the presence of solid carbon The importance of this theory has a particular bearing upon the work to be described

In the art of carburizing, use is commonly made of such words as "catalytic," "atomic," "nascent" and "activated," in an attempt to describe the process   These words are used indiscriminately   For instance, the gas is said to be "catalytic" and carbon to be "nascent," or vice versa   In using these expressions, investigators are confirming the acceptance in their minds of the active conditions of both gas and carbon in the cementation process

Reactions at Metal Surfaces

For many years attention has been directed to the consideration of reactions that occur on metal surfaces   When heated under the influence of certain metals a complex gas will be broken down and one of the constituents thereof usually found to be very active chemically in combining with the metal   The process of nitriding is an example of this type of reaction   In this case ammonia (NH_3) breaks down at the metal surface and the nitrogen which is thus liberated reacts with the surface to form a nitride whereas molecular nitrogen not so liberated is inert and will not react chemically with the metal   Whatever term or terms may be used to describe such reactions, the fact remains that they are highly important and valuable in their commercial applications

Since the metal surface plays so important a part in these reactions, it is evident that any accumulation of reaction products thereon interferes seriously with the progress of the reactions   For this reason it is desirable to remove all such products as rapidly as they are formed in order to bring active gas into contact with the surface and thus facilitate the desired reactions   This is accomplished best by conducting the operation in a continuous manner, thereby causing the reacting gases to pass over the

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* Metallurgical Engineer, Surface Combustion Corporation

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work and carry away the reaction products in the gas stream   The process for continuous nitriding[1] was developed along these lines

The present paper describes another similar development in the process of carburizing, in which the reacting gases are made more effective by their liberation at metal surfaces and in which the products of reaction are removed continuously from these surfaces   In line with our earlier work, this new process has been called "continuous gas carburizing "

HISTORICAL

In approaching the field of carburizing, one must feel the greatest respect for the vast amount of work conducted by previous investigators A list of references of those who have contributed to this subject would be a lengthy one   One thinks of the days when the details of the chemical reactions were being worked out, the many classical discussions as to whether or not solid carbon was the cementing agent, the many exhaustive experiments to clear up these ideas conducted by men whose names are written prominently in experimental metallurgy   The subject has attracted workers of all grades and degrees of ability, and as a result we have a marvelous array of methods, extending from the obscure complex carburizing mixtures of the typical inventor to the phase rule calculations of the erudite   It is doubtful whether any subject in connection with iron and steel metallurgy has been investigated more fully or more elaborately

A good description of the first scientific investigations on the cementation of steel is given by Giolitti in his book[2] on cementation   This book has been a source of much information to all engaged in the art because it is based on the extensive researches of Professor Giolitti   The early work of Baur and Glaessner[3] is of historical interest   The work of Matsubara[4] has given valuable information   In more recent years, the matter of gas carburizing has been studied by Machlet,[5] by Guthrie[6] and by Wilbor and Comstock[7]   These references are given because of their familiarity   They may be considered as dealing with the fundamentals of the art   The work conducted by these men commands our respect

[1] R J Cowan Continuous Nitriding   A New Development *Metal Progress* (Oct , 1930) 93

[2] F Giolitti The Cementation of Iron and Steel   Trans by J W Richards and C A Rouiller, Ed 1, 3   New York, 1915   McGraw-Hill Book Co

[3] E Baur and A Glaessner Gleichgeweite der Eisenoxyde mit Kohlenoxyd und Kohlensaure   *Ztsch f phys chem* (1903) **43**, 354

[4] A Matsubara Chemical Equilibrium between Iron, Carbon, and Oxygen *Trans* A I M E (1922) **67**, 3

[5] A W Machlet Patents

[6] R G Guthrie Gas in the Carburization of Iron and Steel   *Western Gas* (July, 1929) **5**, 32

[7] O J Wilbor and J A Comstock Recent Developments in Gas Carburization *Trans* Amer Soc Steel Treat (1930) **18**, 533

CHEMICAL REACTIONS

In taking up the study of gas carburizing, one is first of all impressed by the fact that carbon dioxide is formed during the carburizing reaction This is shown by the fundamental equations

$$3Fe + 2CO \rightleftarrows Fe_3C + CO_2$$
$$3FeO + 5CO \leftrightarrows Fe_3C + 4CO_2$$
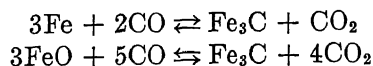
Carbon dioxide is known to be strongly decarburizing in its action The equilibrium diagram shows that a very low concentration of this gas will reverse the direction of the equations so that carbon will be removed from the metal surface rather than added   In a very small area of this diagram the CO_2 formed by this reaction will unite with carbon to form CO by the formula $C + CO_2 = 2CO$, and the system will remain carburizing. If for any reason there should be an increase of the amount of CO_2 in the atmosphere, either locally or throughout, the concentrations quickly carry the system out of the small area referred to and the desired reaction is reversed   This is shown best by reference to the equilibrium diagram given herewith (Fig 1)   The form of this diagram and chart is that used by Clements [8]   The small area referred to is field IV of this diagram. Because of these facts, it would seem to be important to remove the products of reaction as quickly as possible and replace them with gases capable of carburizing   The inability to do this is no doubt one of the limiting factors in the use of solid carburizers and probably accounts for local soft spots frequently found in these carburized cases   On the basis of these facts, it would seem that a continuous process, wherein the carburizing gases were moving through the furnace in the same direction as the work, would be theoretically sound and much to be desired

It is a well-known fact that when any of the hydrocarbon gases are heated in the presence of suitable catalysts they will crack with the formation of solid carbon and hydrogen   The deposition of carbon during carburizing with gas has been considered heretofore a handicap, and these processes have been conducted so as to reduce this to a minimum   Hydrogen also, which comes from the breakdown, is well known as a decarburizer in the presence of slight traces of moisture, and this fact must be taken into account   The problem in connection with the use of gas for continuous carburizing, therefore, takes the form of controlling these two important factors; namely, the deposition of carbon and the liberation of hydrogen

DEPOSITION OF CARBON

The way in which a hydrocarbon gas breaks down is affected by the material with which it is in contact while being heated.   In a silica tube

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[8] F Clements Blast Furnace Practice, 1.   London, 1929   Benn

the reaction is slow, in an iron tube it is rapid   The rate of travel through the tube is also important   The hydrocarbon gases do not break down suddenly into their constituents when being heated, but pass through a progressive series of changes that in some cases is complex The details of these changes are described by Hurd [9]   The effects of different materials on these changes are clearly indicated in this book In our own work, we have found that in the presence of certain alloys, carbon does not form readily from hydrocarbon gases, so that it is possible to pass the gas through a heated muffle made of such alloys without having a copious shower of carbon clog the muffle and destroy the power of the carburizing gas   At the same time, the material to be carburized serves as an excellent catalyst for the breakdown of the gas and brings about the deposition of solid carbon on all surfaces to be carburized, so that in passing continuously through this reaction zone these surfaces become uniformly covered with a coat of solid carbon   In other words, by the means indicated, we have been able to accomplish a selective precipitation of carbon on surfaces that we desire to carburize

EFFECT OF HYDROGEN

This regulated breakdown of the hydrocarbon gases furnishes a means also for controlling the decarburizing power of hydrogen, which is liberated with the carbon in this breakdown   Any high concentration of hydrogen would completely ruin the process unless its effect were neutralized   In continuous carburizing, this hydrogen would accumulate in the discharge end of the muffle and decarburize the previously carburized surface. It has been found, however, that a comparatively small percentage of methane (CH_4) in an atmosphere of hydrogen is sufficient to prevent decarburization   This matter has been investigated carefully by Sykes[10] and the details of the equilibrium given.   In a discussion of this paper by Fink,[11] the following interesting comment is made "It might be of interest to note that this equilibrium was used to prepare all of the specimens used in the work done by Professor Campbell from 1922 until his death "   By means of this equilibrium, it is possible to control the carbon content of the case produced   This is done by controlling the methane (CH_4) content of the effluent gases, for there is a definite CH_4 content in equilibrium with each carbon content desired.

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[9] Hurd   The Pyrolysis of Carbon Compounds   Amer Chem Soc   *Monograph* 50

[10] W P Sykes   Carburizing Iron by Mixtures of Hydrogen and Methane   *Trans* Amer Soc Steel Treat (1927) **12**, 737

[11] W L Fink   Discussion on Carburizing Iron by Mixtures of Hydrogen and Methane   *Trans* Amer Soc Steel Treat (1927) **12, 757**

Methane (CH_4) is formed as one of the reaction products in the progressive pyrolysis of higher hydrocarbons   Being the first member of the aliphatic series, it is much more stable under heat than the higher

AUTHORITIES–

$2\,CO \rightleftharpoons C + CO_2$ BOUDOUARD

$Fe O + CO \rightleftharpoons Fe + CO_2$
$Fe_3 O_4 + CO \rightleftharpoons 3FeO + CO_2$
$3FeO + 5CO \rightleftharpoons Fe_3 C + 4CO_2$ MATSUBARA
$3Fe + 2CO \rightleftharpoons Fe_3 C + CO_2$
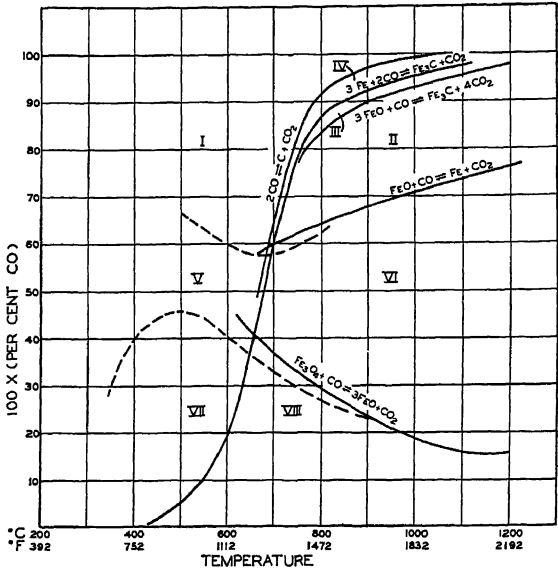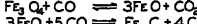
THE DOTTED LINES ARE THOSE OF BAUR AND GLAESSNER

REACTIONS		$2\,CO$ $\rightleftharpoons$ $C + CO_2$	$FeO + CO$ $\rightleftharpoons$ $Fe + CO_2$	$Fe_3O_4 + CO$ $\rightleftharpoons$ $3\,FeO + CO_2$	$3FeO + 5CO$ $\rightleftharpoons$ $Fe_3C + 4CO_2$	$3Fe + 2CO$ $\rightleftharpoons$ $Fe_3C + CO_2$	SOLID END–PRODUCTS IN EQUILIBRIUM
THE ARROWS INDICATE THE DIRECTION, IN WHICH THE REACTIONS OCCUR IN THE FIELDS II ETC	I	→	→	→	→	→	Fe_3C AND SOLID C
	II	←	→	→	←	←	METALLIC FE WITHOUT SOLID C
	III	←	→	→	→	←	METALLIC FE WITHOUT SOLID C
	IV	←	→	→	→	→	Fe_3C WITHOUT SOLID C
	V	←	←	→	DATA INCONCLUSIVE	DATA INCONCLUSIVE	FeO AND SOLID C
	VI	←	←	→	←		FeO WITHOUT SOLID C
	VII	→	←	←	DATA INCONCLUSIVE	DATA INCONCLUSIVE	Fe_3O_4 AND SOLID C
	VIII	←	←	←	DATA INCONCLUSIVE	DATA INCONCLUSIVE	Fe_3O_4 WITHOUT SOLID C

FIG 1 —TEMPERATURE-CONCENTRATION DIAGRAM OF IRON-CARBON EQUILIBRIA AT CONSTANT PRESSURE OF ONE ATMOSPHERE ABSOLUTE

members of the series   During the pyrolysis of these higher members methane is usually found as the last step before the final breakdown. It is apparent from this that when the hydrocarbon breakdown is carried

on selectively, as described in a preceding paragraph, only a part of the total gas volume is broken down completely while the remainder serves as a protection against decarburization by hydrogen in the latter stages of the process   Without taking advantage of the known effects of catalysts on these gas reactions, it would be impossible to conduct the operation in this way

Effect of Carbon Dioxide

Having discovered how to obtain selective deposition of solid carbon on metal surfaces and at the same time control the decarburizing power of hydrogen, the next step for consideration dealt with methods of controlling the concentration of carbon dioxide

In an earlier part of the paper, attention has been called to the characteristics of CO_2 If not removed at once from the reacting surface, it will bring about decarburization even more rapidly than hydrogen itself   To prevent this it must be diluted with a large admixture of carbon monoxide (CO)   The equilibrium conditions that govern these reactions are well known and are given in the standard texts   A very good critique of the whole subject is given by Ralston [12]   These texts indicate definitely the amount of CO_2 in equilibrium with any carbon concentration at any temperature considered.   The details are given in Fig 1.   The problem that confronts us in continuous gas carburizing is one of insuring the gas mixture of CO and CO_2 that is desired

Attention has been called to the fact that the hydrocarbon gases are broken down in this process in such a way as to cause a selective deposition of solid carbon on the surface of metal to be carburized   The reason for this will be apparent from the following facts   In order to obtain the mixture of carbon monoxide and carbon dioxide to allow proper carburizing to take place, there is introduced with the hydrocarbon gas a certain proportion of CO_2 in the form of flue gas.   At a temperature corresponding to the minimum carburizing temperature, this reacts with carbon to form carbon monoxide, as shown by the equation $C + CO_2 = 2CO$ Inasmuch as the solid carbon found in the system is largely that adhering to the surface of parts to be carburized, the carbon dioxide must react with this carbon right at the metal surface at carburizing temperatures under conditions that are ideal for rapid carburizing   The carbon dioxide which is produced by carburizing $3Fe + 2CO = Fe_3C + CO_2$ finds itself also in contact with carbon on the metal which reacts immediately to reduce this to the monoxide and so continue the carburizing cycle   At the same time the excess solid carbon is reacting with carbon dioxide of the flue gas, thus maintaining the excess of monoxide necessary in the atmosphere to insure the progress of the reactions in the right

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[12] O C Ralston   Iron Oxide Reduction Equilibria   U S Bur Mines *Bull* 296 (1929)

direction. It is significant that this reaction is taking place also at the metal surface where the carbon monoxide produced is in the most effective form for carburizing.

These reactions have been taken up individually and described as if they were separate and unrelated to one another. Such is not the case. It must be borne in mind that all these reactions are going on at the same time and that they have been separated and accounted for in this way only for purposes of description. The method of control of the process is very simple, however, and will be taken up later.

EXPERIMENTAL PROCEDURE

Having determined the feasibility of the process from a theoretical standpoint, we will now follow the development of these ideas along practical lines until they evolve into a process for continuous gas carburizing.

Our first run was in a small laboratory furnace. We raised the temperature to 1350° F. for 2½ hr., using an atmosphere of natural gas and carbon dioxide. Under these conditions the sample of steel became covered with a deposit of carbon. The natural gas was then turned off, the CO_2 continued and the temperature raised to 1750° F. for 3½ hr. This was done to show the effect of CO_2 and to find out how far it was possible to go in its use before causing decarburization. The results are shown in Fig. 2. The first thing to be noticed is the decarburized edge, which is proof of the fact that the flow of CO_2 had been
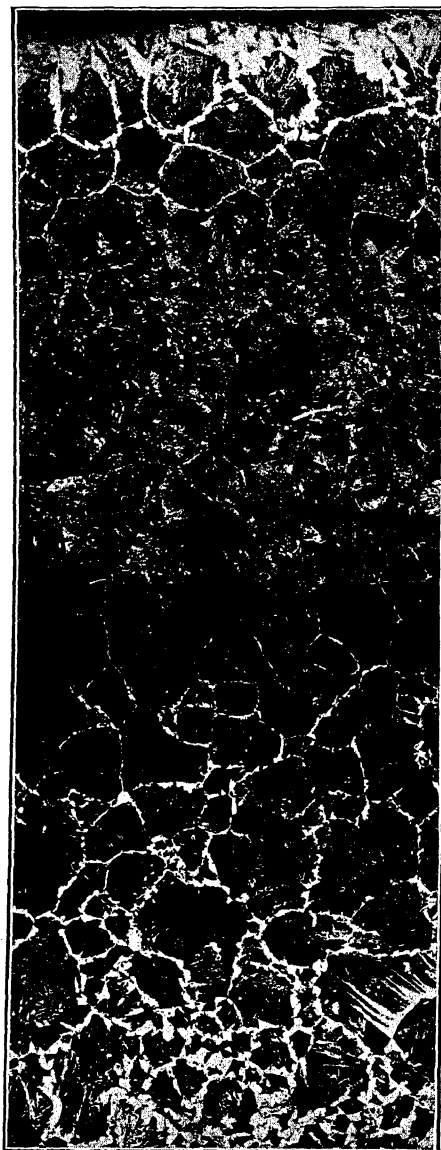
FIG. 2.—EFFECT OF REACTION BETWEEN FREE CARBON AND CARBON DIOXIDE AT 1750° F. NATURAL GAS USED WITH PURE CO_2. × 100.

Reduced 25 per cent; original magnification given.

continued too long   However, a very deep case had been produced with satisfactory diffusion between case and core   A number of similar tests were made in the laboratory   By this means it was clearly proved that the reaction between carbon and carbon dioxide at the metal surface was effective in causing rapid carburization of the steel   Attention must be called to the fact that the carbon penetration is about 0 065 in and that this was produced by holding only 3½ hr at carburizing temperature

The next move was to construct a furnace with a muffle 12 ft long, with temperature controls for maintaining different zones in the furnace All subsequent work has been done in this furnace   Natural gas, propane, butane and acetylene have been used for carburizing, all in conjunction with flue gas   The flue gas consisted of the products of combustion of a gas-fired furnace and for most of the work had the following analysis 8 5 per cent CO_2, 0 0 per cent O_2, 3 0 per cent CO, in addition to water vapor and possibly some sulfur compounds   It was necessary to dehydrate the flue gas before using it   With this equipment, a great many tests have been made to enable us to work out the details of the process The unit was large enough for semicommercial work and cam shafts and similar parts have been carburized in it   The outcome of these tests has been the development of a very simple process that will now be described in detail

Continuous Gas-carburizing Process

The process as conducted may be considered as including three zones in which the essential reactions are as follows the first zone that of carbon deposition, the second that of active carburization; the third that of carbon diffusion

The carburizing gas with a large admixture of flue gas is forced into the muffle so as to flow through in the same direction as the work to be carburized   Under the catalytic effect of the steel to be carburized, the hydrocarbon gas cracks in the first low-temperature zone of the furnace The breakdown of this gas is not complete but only sufficient to cover the work uniformly with a deposit of free carbon which adheres to the work This breakdown is regulated by the rate of flow of the gas through the first zone, which in reality is but a slightly elongated preheat zone   The deposition of this carbon is so regulated, as described above, that it occurs on the surface of the work rather than on the muffle walls

In the second, or full-temperature zone of the furnace, the carbon dioxide of the flue gas becomes effective   Previous to this, the flue gas has served only as a desirable diluent of the carburizing gas   Now it becomes active, because at these temperatures the reaction is reversed and goes on as follows $C + CO_2 = 2CO$ It is in this zone that active carburizing takes place   The reaction is very energetic, possibly assisted by the presence of some sulfur compound from the flue gas, but probably

due to the catalytic action of CO_2, which is known to have an important effect on these reactions   In this way, the essential carburizing reactions are obtained right at the surface of the metal   This was referred to in the introductory part of paper and is the same principle that has been of such great industrial importance in other connections   It is a well-known fact that rapid carburizing is apt to cause a sharp demarcation between case and core, so that if the process stopped here there would be trouble from exfoliation in service   For this reason, there must be a third, or diffusion, zone

In the diffusion zone of the furnace the atmosphere is of great importance   It must contain a minimum of CO_2 and not less than a definite amount of CH_4, depending on the carbon content desired in the metal case   The process is controlled by regulating the composition of the gases in this zone   Too much CO_2 indicates that too much flue gas is being used   Too little methane indicates too little carburizing gas   By these indications it is possible to regulate the carbon content desired in the case   Also, under the conditions existing in this zone, the carbide case diffuses toward the inner core so that the carbon concentration lowers gradually toward the core   After sufficient time in this zone the work may be further cooled or quenched, as desired

Results Obtained

To illustrate the different zones in the furnace and show the effects of the reactions taking place in each zone, a series of photomicrographs has been taken of specimens throughout the furnace length, as they existed in the furnace after the continuous operation had been brought to a sudden stop and the furnace cooled as rapidly as possible

Fig 3 was taken from a specimen 3 ft from the entrance to the muffle It shows clearly the deposition of carbon on the surface and the beginning of carburization   The temperature at this point was about 1450° F Fig 4 was taken from a specimen in the center of the carburizing zone where the temperature was 1650° F   The case and core are defined rather sharply which indicates insufficient carbon diffusion   Fig 5 represents the completed case after having passed through the diffusion zone of the furnace   In this zone, the temperature drops gradually from the maximum to about 1400° F.   Attention is called to the fine diffusion between case and core

The ability to control the carbon content of the case is well represented in Figs 6 to 9   Fig 6 shows a hypoeutectoid case produced by a certain gas flow   Attention is called to the uniformity of this case and absence of decarburization   With no other change than an increase in flow of the carburizing gas, the same temperature cycle produced the case shown in Fig 7   Again the uniformity of case and absence of decarburization is to be noted.   The case is much higher in carbon, in this instance   Fig 8
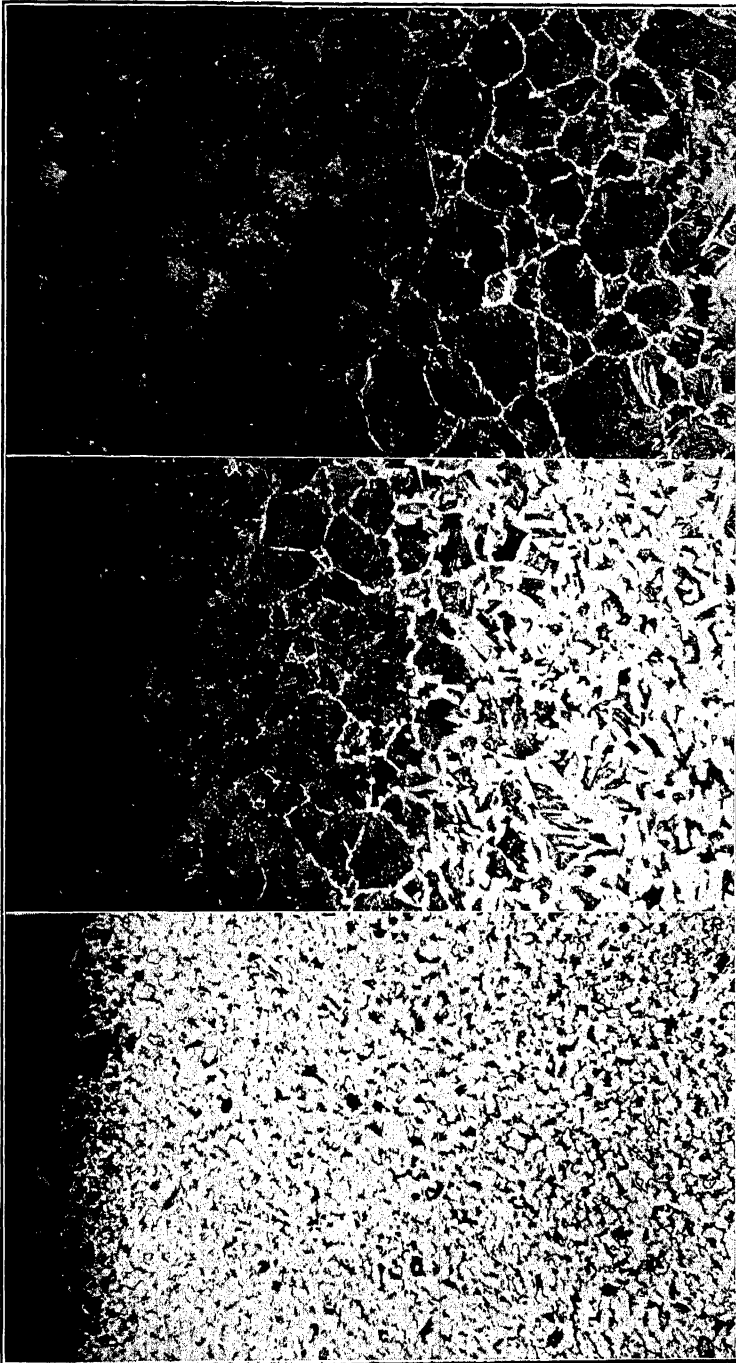
FIG. 3.

FIG. 4.

FIG. 5.

FIGS. 3-5.—PROGRESS OF CARBURIZATION. ALL × 100.

FIG. 3.—BEGINNING OF CARBURIZING ZONE, SHOWING FREE CARBON ON SURFACE.
FIG. 4.—CENTER OF CARBURIZING ZONE, SHOWING IMPROPER DIFFUSION BETWEEN CASE AND CORE.
FIG. 5.—END OF CARBURIZING ZONE, SHOWING SATISFACTORY DIFFUSION.
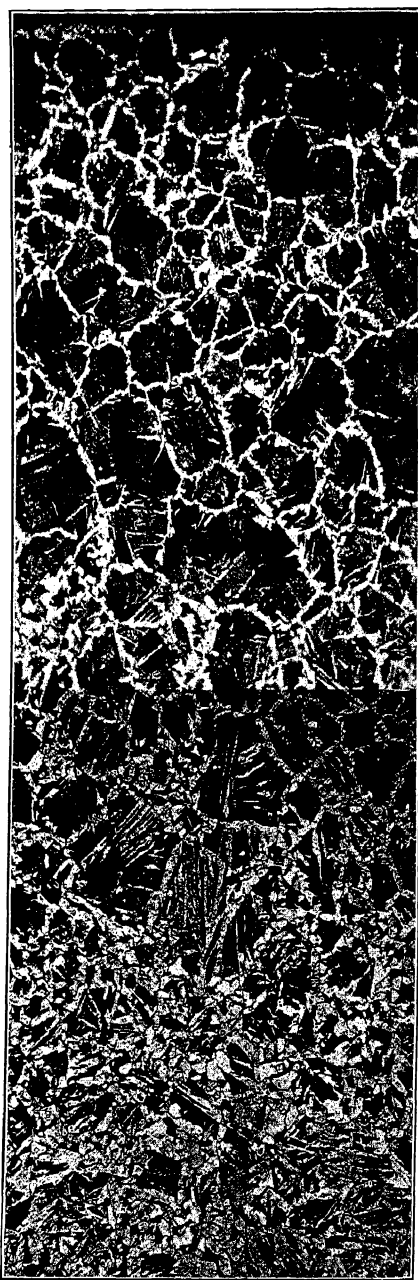
FIG. 6.—HYPOEUTECTOIDAL CASE. ✕ 100. (REDUCED 25 PER CENT; ORIGINAL MAGNIFICATION GIVEN.)
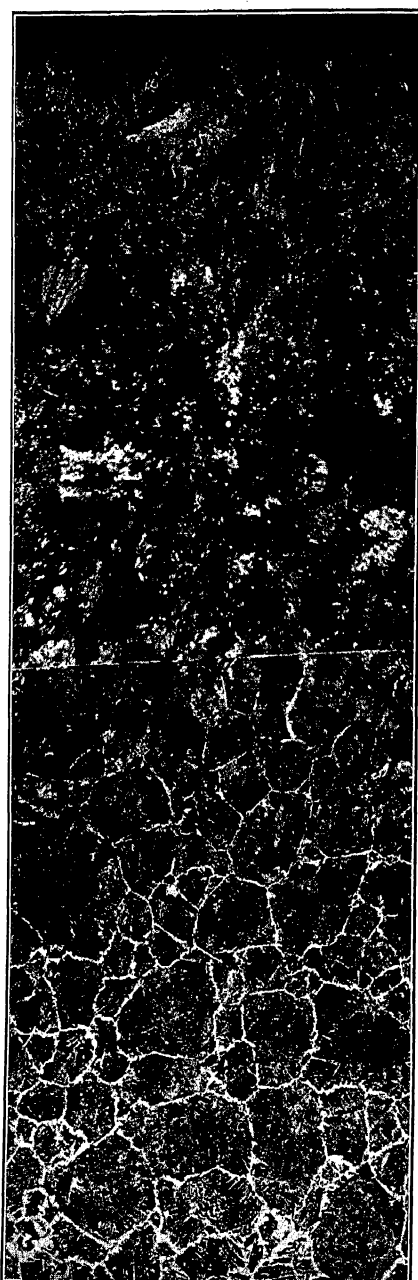
FIG. 7.—EUTECTOIDAL CASE. ✕ 100. (REDUCED 25 PER CENT; ORIGINAL MAGNIFICATION GIVEN.)

FIG. 8.—HYPEREUTECTOIDAL CASE. ×
100. (REDUCED 25 PER CENT; ORIGINAL
MAGNIFICATION GIVEN.)

FIG. 9.—HYPEREUTECTOIDAL CASE. ×
100. (REDUCED 25 PER CENT; ORIGINAL
MAGNIFICATION GIVEN.)

shows a hypereutectoidal case and Fig. 9, a different type of hypereutec-
toidal case, produced by different flue-gas and hydrocarbon-gas ratios.

One interesting feature of this work has been the uniformity of results
obtained. As long as the gas flow is constant, all other conditions remain-
ing constant, there will be constancy in the results. Throughout all of
this work there has been found no indication of soft spots or decarburiza-
tion. Regardless of the gas mixture used, the case formed has been uni-
form not only in the individual piece but throughout the series.

A good illustration of the course of these reactions is shown in the
photograph of a cam shaft carburized by this process (Fig. 10). As is
common practice, some of the parts of this shaft were covered by copper-
plating to prevent carburization. When the shaft was removed from the
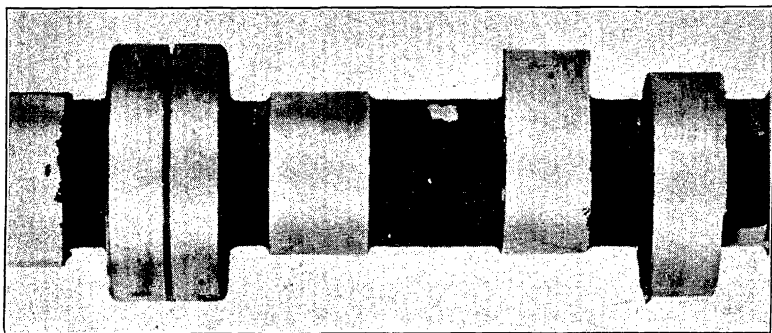
FIG. 10.—COPPERPLATED CAM SHAFT AS TAKEN FROM FURNACE.
Showing carbon deposit on plated portions and absence of carbon on carburized
cams.

furnace, the parts copperplated were covered with soot, whereas the parts
not plated were almost free from soot. Fig. 10 shows the shaft just as it
was taken from the furnace. Apparently free carbon had deposited over
the whole shaft in the first zone of the furnace, but during the subsequent
reactions the carbon on the parts not protected by copperplating was
absorbed by the metal, whereas the copperplated parts, where no cemen-
tation took place, retained much of the original carbon deposit. This
particular shaft had a case of 0.080 in., which had been produced by
5 hr. at 1750° F.

A study has been made of carburizing rates as obtained in typical
industrial installations to obtain data for comparison with the rate
obtained in these tests, as follows:

PLANT NUMBER	RATE PER HOUR, IN.	DEG. F.
1	0.0033	1680
2	0.005	1650
3	0.0044	1750
4	0.0062	1725
6	0.006	1650

These results are based on the use of solid carburizers For comparison, the results of plant 4 will be used, as these seem to represent the best practice In the continuous process, a case is obtained of 0 045 in in $2\frac{1}{2}$ hr at 1725° F , or a rate of 0 018 in per hour, which is about three times the rate shown above of the usual practice as obtained by box carburizing A case of 0 035 in is obtained by holding 3 hr at 1650° F This indicates clearly that the process is efficient in the rate of carburization obtained

The process as conducted has the merit of being clean This is something new and quite revolutionary in connection with work of this kind If the proportions of the gases used are properly regulated, it is possible to bring the work from the furnace in a bright condition, almost as bright as when it enters The deposition of carbon takes place inside the muffle and there is no smudge outside If desired, the work may be brought out with a covering of carbon which will serve as additional protection against decarburization during the subsequent reheating for quenching By this means there is provided a control of the operation to meet specific requirements

A furnace has been developed for commercial work based on the principles described in this paper, which makes it possible to conduct the process in a suitable mechanical manner

SUMMARY

The details of the process for continuous gas carburizing as developed in this paper may be summarized as follows A hydrocarbon gas is mixed with flue gas containing CO_2 and introduced into a muffle containing work to be carburized, so as to move through in the same direction as the work In the preheat zone of the furnace the hydrocarbon gas begins to break down, so that the work to be carburized soon becomes covered with a deposit of precipitated carbon In the carburizing zone, active carburizing takes place because of the chemical reaction between this deposited carbon and carbon dioxide, which at these temperatures becomes effective. In the subsequent diffusion zone, the carbide case formed is allowed to penetrate toward the core to obtain proper gradation of properties The metal, in passing progressively through these three zones, becomes carburized as desired by a proper regulation of the time, the gas flow and proportioning of the mixture, so that any carbon composition desired on a case may be consistently obtained After completing this cycle, the metal may be quenched or cooled slowly as desired This provides a new process for carburizing steel, which is different from anything before attempted.

The advantages of this process are as follows
1. Control of carbon content of the case produced
2. Uniformity of results

3 Rapidity of carburization
4 Excellence of diffusion between case and core
5 Cleanness of operation.
6 Continuous operation.
7 Simplicity of control

ACKNOWLEDGMENTS

DISCUSSION

(A B Kinzel presiding)

R A RAGATZ, Madison, Wis (written discussion) —Mr Cowan appears to have developed a carburizing process that has possibilities of commercial application, particularly so in view of the increased availability of natural gas resulting from the recent rapid development of pipe lines   The process is a sound application of the theoretical principles involved in the pyrolysis of carbon compounds, the equilibrium relationship between carbon and its oxides, and the reaction between steel and carbon monoxide

However, some of the statements made in the section on Chemical Reactions require a somewhat more detailed treatment for the sake of clarity   The author justly emphasizes the need for keeping the carbon dioxide concentration in the gaseous phase low, but somewhat overstates the case   It is stated that if the carbon dioxide concentration lies below the curve labeled $3Fe + 2CO \rightleftarrows Fe_3C + CO_2$ (below field IV) "the desired reaction is reversed" and "carbon will be removed from the metal surface rather than added "   This appears to signify that if the carbon dioxide concentration in the gaseous phase lies below field IV, carburization cannot proceed at all   That this is not true is shown by the somewhat more detailed explanation of the situation, as follows

If the carbon dioxide concentration lies within or above field IV, and if the temperature is above Ac_3 for the particular steel being carburized, the metal will absorb carbon and the outer layer in contact with the gas will pass through several successive stages   First it will consist of unsaturated austenite, becoming progressively richer in carbon   Ultimately the austenite will become saturated and free cementite will appear   The quantity of free cementite will increase progressively, while the quantity of saturated austenite will decrease   Theoretically, the metal ultimately will be converted into pure cementite   However, the well-known instability of cementite probably will assert itself before this stage is reached, and pure carbon will form in the metal   If the carbon dioxide concentration is below field IV, and if the temperature is above Ac_3 for the particular steel being carburized, the metal can still undergo carburization within certain limits   The outer surface in contact with the gas will be completely austenitic but at no time will any free cementite be present   The equilibrium relationships between gas composition, temperature, and carbon con-

tent of the austenite have been carefully worked out by Johannson and Von Seth,[13] and their work should be consulted for details

In view of the fact that one of the essential features of the process is deposition of powdered carbon on the steel surfaces, the writer would like to inquire whether uniform results are obtained on surfaces of various degrees of inclination   That is, if a cube of steel were passed through the carburizing furnace, how would the case depths of the top, bottom and vertical surfaces compare?

The writer wishes to inquire whether any gas analyses were made at various regions in the furnace, when it was in continuous operation   Such figures, if available, would be of interest

The results obtained are dependent upon the proportions of flue gas and natural gas   Will the authors briefly describe the mechanical devices that they found satisfactory for mixing and proportioning the two components of the gas passed into the carburizing chamber?

B B BECKWITH, Detroit, Mich (written discussion) —Mr Cowan has attacked an old problem in a new way, that of obtaining a satisfactory case in as short a time as possible   The use of gas for carburizing is old, but the application of it to a continuous process is new

Some of the samples of S A E No. 1015 which were carburized in the furnace described in the article were forwarded to me for examination   They were remarkably free from carbon deposit and showed 0 065 to 0.080 case   Some were eutectoid composition at the surface and the others on a different run were slightly hypereutectoid (the diffusion between case and core was gradual)   All samples hardened satisfactorily with a water quench.

From the description of the process the control consists of maintaining a definite ratio between the CO_2 of the flue gases and the CH_4 This would necessitate more careful technical supervision of the actual carburizing operation than is common practice at the present time with pack carburizing.

There are possibilities in this process and I shall be much interested in the results obtained from a production furnace constructed along the lines of the present experimental unit.

E F DAVIS, Muncie, Ind (written discussion) —Mr Cowan is to be complimented upon the manner in which he has discussed the theoretical phases of gas carburizing and he is also doing some real pioneering in the field of practical metallurgy It is my opinion that pack hardening methods and the use of solid carburizers will be obsolete within the next 10 years.   Although continuous furnaces for pack methods have improved this process considerably, it is still too crude, too uncertain in results, and too costly.   The continuous gas furnace is an advancement no metallurgist can afford to ignore.

Our knowledge of the C, CO and CO_2 interchanging reactions is gradually becoming more definite   No longer are the peculiar events occurring on the inside of a carburizing box beyond our comprehension   The atomic interchange of C, CO and CO_2, the phenomena surrounding the reversal of these molecules and the properties of each dominant gas are now more thoroughly understood   If Mr Cowan's new furnace is able to harness these gases, control the chemical reactions and produce an atmosphere of the desired composition in the various carburizing zones, he has accomplished a real development in furnace design.

There is always a possibility of certain elements being introduced with the gas which may upset any established equilibrium.   Assuming that methane or natural gas was used as the carburizing medium, and that this gas should become diluted with

[13] Johannson and Von Seth: *Jnl.* Iron and Steel Inst (1926) **114,** 295

air, coke-oven gas, sulfur dioxide or nitrogen compounds, such as ammonia gas, would not this require an entire readjustment of the gas stream? How would we anticipate the appearance of these interfering substances? Do they actually change the characteristics of the operation as Mr Cowan has outlined it?

When carburizing by gas by the continuous process it is necessary to perform the actual carburizing in a muffle arrangement which, of course, means that the work is heating by radiation and a high temperature differential exists between the combustion chamber and muffle When the furnace is empty there would be a tendency for the muffle walls to overheat and when it was charged the cold work would undercool the walls This is a common defect with many types of continuous muffle furnaces, such as the spiral muffle used in ball hardening I wonder whether Mr Cowan has provided against the possibility in temperature variation which, of course, would also be a factor in case depth

A B KINZEL, New York, N Y —I wonder if this matter of control of the gases, the possibilities of commercially using premixed synthetic gases, has been considered I refer to the propane type, for example, which is distributed in cylinders The analysis is well controlled, so that some of the difficulties which might arise in the atmosphere control would be avoided

W J MERTEN, East Pittsburgh, Pa —I wonder whether the author is not suspicious as to the theoretical calculations of the chemistry of the process? Considering the solid carbon coating on the camshaft, which does not gasify, it seems logical to conclude that there may be other factors involved in the solution of carbon in iron including the formation of CO_2

R. J. COWAN (written discussion) —The discussion of this paper is gratifying in that it deals with both the theoretical and practical aspects of the subject The words of commendation are much appreciated and the points raised serve to clarify the whole matter

Mr Ragatz directs attention particularly to some theoretical considerations regarding the effect of increasing amounts of CO_2 on carburizing His discussion is a valuable addition to the paper In writing as I did I had in mind the usual temperatures of carburizing practice, but it is a fact that much greater amounts of CO_2 may be present at lower temperatures, which is shown by the shape of field IV as given The exact relationship between the gases involved and the carbon content of the steel are shown by the reference given and by others These facts are well known. In the paragraph referred to it was intended to emphasize the importance of removing these reaction products as quickly as possible

In regard to the uniformity of carbon deposition, it may be pointed out that this deposition is dependent on the catalytic effect of iron on the hydrocarbon gas whereby all exposed surfaces of iron become covered by carbon. A piece of steel removed from the carbon deposition zone is always covered uniformly with carbon regardless of its shape The cam shaft shown in the paper is an illustration of this

Gas analyses have been taken of effluent gases but none from the different reaction zones. The control of the process is effected by controlling the effluent gases This is done by regulating the proportions of incoming gases, which is accomplished by passing through suitable indicating meters or through flow meters. The gases are passed into a common header and enter the furnace directly without going through any mixing chamber

Mr. Beckwith also asks about the method of control of the incoming gases. It is not necessary to keep adjusting this gas flow After the ratio of hydrocarbon to flue gas is set the flow is maintained constant throughout the cycle by a constant differential over an orifice By this means the control is made very simple

Mr Davis asks about the effects of certain impurities on the essential gas reactions As long as these diluents are in small proportions they will not affect the reactions in any important way   For instance, air would immediately be burned to CO in the presence of so much carburizing gas, and this constituent is normal to the process, coke-oven gas would also yield normal constituents on heating, except in the case of high sulfur, which would yield SO_2 after combustion, but in either case furnish a catalyst that is thought to be desirable for carburizing   Ammonia gas will break down quickly to N_2 and H_2 when heated, both of which are present in the furnace muffle   It is not believed that these substances will actually affect the essential characteristics of the main reactions

Mr Davis asks also about the drifts and lags that are to be looked for when heating metals in a muffle   This has been taken care of by properly regulating the heating rate in accordance with experience gained from similar applications   A number of furnaces have been in service for years with satisfactory temperature regulation and there ought not to be any trouble from this source in its effects on case depth

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